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THE EFFECT OF SOLID PHASE REACTIONS ON THE BALLISTIC PROPERTIES OF PROPELLANTS

By Willfred G. Schmidt

September 1970

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Prepared under Contract NAS1-9463 by

Aerojet Solid Propulsion Company
Sacramento, California

For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

The combustion of NH_4ClO_4 composite propellants has been studied between 15 and 3000 psi. The emphasis in the program has been on determining the mechanisms by which the fuel components influence the burning rate of the composites. In order to have flexibility in the choice and concentration of the fuel component all combustion experiments were performed with pressed powder strands. The fuels studied included those which affected the combustion mechanism of the composite primarily through their effect on (1) the oxidizer decomposition mechanism and (2) the composite surface temperature. The combustion of pure and doped NH_4ClO_4 was studied using both pressed powder strands and pressed end burning motor grains. The experimental approach has been essentially a chemical one with emphasis on perturbing those reactions which occur on or immediately adjacent to the surface (zone of influence) of the composite. A hypothesis is offered to explain how the various physical and chemical properties of the fuel affect the combustion of an NH_4ClO_4 composite propellant. In addition, the isothermal decomposition of phosphate and chlorate doped AP was studied, between 200 and 300°C, using thermogravimetric techniques.

THE EFFECT OF SOLID PHASE REACTIONS ON THE BALLISTIC PROPERTIES OF PROPELLANTS

Willfred G. Schmidt
Aerojet Solid Propulsion Company, Sacramento, California

SUMMARY

An investigation into the combustion mechanisms of ammonium perchlorate-fuel composites (pressed powder strands, 12 cm . cm^2) has led to the conclusion that the rate determining reactions occur in a narrow zone near, and including, the surface of the composite. The reaction rates in this 'zone of influence' are a function of the temperature in this region, which in turn is a function of the sum of the heat flux to the surface, the heat losses from the surface and the net heat from all reactions, both endothermic and exothermic, occurring in this region. There are several ways in which the fuel component may affect the combustion rate of the composite. If the fuel or its products do not react with the oxidizer or its products in this zone of influence the fuel will still affect the temperature in this region by the net endothermicity or exothermicity of its degradation and volatilization mechanisms. The fuel may decompose to form products, such as hydrogen or a carbon char, which can further react close to the surface of the composite rather than in the gas phase at a significant distance from the surface. The fuel can decompose to form products such as ammonia or water which may perturb the NH_4ClO_4 decomposition mechanism, or the fuel may directly react with the oxidizer in a condensed phase or heterogeneous reaction. The various ways by which the fuel can affect combustion are not mutually exclusive but rather several of these effects may be operating in any given composite.

Using 38 mm diameter pressed end burning grains, it was shown that the burning rate pressure exponent for pure AP was positive and constant between 1200 and 3000 psi. Isothermal kinetic studies have shown that phosphate negatively catalyzes the low temperature NH_4ClO_4 decomposition while chlorate is a positive catalyst for this decomposition. Despite causing significant changes in the rate of the low temperature decompositions these materials have only a limited effect on the NH_4ClO_4 combustion rate.

INTRODUCTION

This program was undertaken to investigate the reactions and mechanisms of decomposition which occur in the substrate at or below the burning surface of perchlorate-containing propellants in order to determine their contribution to the overall processes involved in the deflagration and combustion of solid propellants. The work has been carried out along two parallel but interdependent paths, (1) to determine which solid phase reactions contribute to the rate of the overall combustion process, and (2) to determine mechanisms for those reactions which affect the rate of the combustion process. The primay emphasis has been on establishing relationships between the properties of the fuel component and the combustion characteristics of NH_4ClO_4 - fuel

composites. In the previous investigations, NAS1-6323 and NAS1-7816, the fuel component was held constant while changes in the combustion characteristics of composites were affected by modifying the properties of the oxidizer. In addition to this major objective,work has continued on the decomposition and combustion of both pure and doped NH_4ClO_4.

Three recent reviews (References 32, 33 and 34) have covered much of the data not only on AP decomposition but also on the combustion of AP and AP-fuel composites. There is virtually no systematic work reported in the area of fuel pyrolysis, under combustion conditions, and its effect on the combustion of AP composites. The work of Powling (Reference 30) does show that the nature and the amount of the fuel component has a strong effect, especially at higher pressures, on the combustion rate of an AP composite. However, there was no simple relationship between a given property of the fuel, such as volatility, and its affect on the combustion rate.

Since previous work (Reference 6) has led to the conclusion that condensed phase, including surface, reactions are important in the combustion of NH_4ClO_4 an attempt to understand the effect of the fuel component requires that attention be focused on those reactions occurring close to or on the surface of the composites. This zone, "zone of influence" (Reference 29) is relatively narrow and does not lend itself to direct measurements but must be probed by chemical means. That is, a hypothesis for combustion is continually tested, and modified when necessary, by using chemical means to perturb reactions in the 'zone of influence'. Sometimes these chemical changes affect combustion in an indirect manner such as altering the temperature in the reaction zone while at other times they may directly cause a perturbation in the rate controlling decomposition process.

Although a great many studies have been undertaken, as indicated in the three reviews (References 32, 33 and 34), there is still no general agreement on the AP decomposition or combustion mechanisms. The low temperature AP decomposition has been investigated in this program with the idea of making comparisons with previous work on the basis of the directly measured decomposition rates rather than on the basis of such derived values as activation energy. The effect on combustion of both positively and negatively catalyzing the AP low temperature decomposition mechanisms was investigated using pressed powder strands. The work in all areas was divided into two sections, (1) decomposition studies which investigated the properties of the materials as heat is applied to them, and (2) studies of the materials under actual combustion conditions (no external energy added to the system). The two studies are complimentary and relationships (both positive and negative) were determined between the decomposition and the combustion processes.

When necessary, materials were synthesized to meet the demands of the program. The experimental work utilized several different thermogravimetric balances, differential thermal and scanning calorimetric equipment. A pressure vessel previously constructed (Reference 1) allowed differential thermal

analysis to be run at pressures up to 2000 psi. A previously constructed set of dies was used to obtain pressed powder strands and during the course of this program a set of dies was constructed which made it possible to compact pressed powder grains 38mm in diameter. All burning rate measurements were obtained by the use of pressure time instrumentation.

PROCEDURES, RESULTS AND DISCUSSION

I. EXPERIMENTAL

A. EQUIPMENT

All ambient pressure differential thermal analyses (DTA) were performed with a commercial instrument (duPont 900). An attachment also allowed isothermal differential thermal analysis. Pressure DTA work used the controls and recording section of the above instrument in addition to a remote cable which carried the electrical leads to a pressure vessel (Reference 1). Due to heat losses to the pressurized atmosphere, heating rates at pressures above 1000 psi were maintained by the use of an auxiliary heater, which consists of a nichrome wire wound into an asbestos jacket, around the sample block. Quantitative data at ambient pressure were obtained with a differential scanning calorimeter (Perkin-Elmer DSC-1B).

Thermogravimetric work was performed on three different instruments. For corrosive gas atmospheres, an apparatus was used which consisted of a quartz spring in an oven heated tube; measurements were made with a cathetometer. Isothermal measurements under air or nitrogen atmospheres were made with a commercial automatic recording thermogravimetric balance (Ainsworth). Non-isothermal measurements were made with an attachment to the DTA (duPont 950). Temperature control with the Ainsworth balance is $\pm 2°C$ at 300°C with the temperature being measured by a Pt-Pt·10% RH thermocouple located immediately below the glass wool sample holder.

Burning rates were obtained with pressed powder strands and pressed powder end burning grains. A strand die and press frame, designed and built at Aerojet was used in compressing the materials for the strands. To minimize the density gradient in the strand, the strand is pressed perpendicular to the long axis, i.e. the powder depth is less than one centimeter. The dimensions of the compacted strand are 0.95 cm x 0.95 cm x 12.2 cm. From this, four individual burning rate versus pressure points were obtained by cutting the strand into four approximately equal lengths; testing was done in a closed bomb using pressure-time instrumentation. The end burning grains were obtained by compaction in a 3.8 cm diameter circular die. The depth of the grain could be varied; however, it was generally maintained at $\sim$1.2 cm to minimize the density gradient. The compacted grains were tested in an end burning motor configuration and the burning rate determined with pressure time instrumentation.

B. SAMPLE PREPARATION OF AN ANALYSIS

The ammonium perchlorate (AP) used in the isothermal studies was material that had been twice recrystallized from water. This recrystallized AP was also used as the starting material for the doped AP crystals.

1. Doped AP

a. AP Containing Phosphate

The following is the procedure used in the preparation of AP containing a small percentage of phosphate. In this report phosphate is taken to mean the sum of $H_2PO_4^-$, $HPO_4^=$, and $PO_4^{\equiv}$ since the exact form in the crystal is not known. AP is dissolved in water at ∿60°C (AP to H_2O ∿1:2) and $(NH_4)_2HPO_4$ is added and stirring continued until all salts are dissolved. The temperature is kept between 50 and 60°C while the solution is filtered after which the filtrate is cooled to ∿5°C in an ice bath. The crystals are removed by filtration and dried in a vacuum oven at 50°C overnight. Phosphate is analyzed for by the method of Gee and Deitz (Reference 2). It was experimentally determined that the AP did not affect this method of analysis which is a spectrophotometric one utilizing a mixed molybdatemetavanadate solution to develop the color. Measurements are made in the region of 350-400mμ. The analysis is sensitive to the acid concentration which must be reproducibly controlled. A calibration curve was established with known amounts of $(NH_4)_2HPO_4$. From this curve it was determined that the previously described procedure for making AP containing phosphate results in a crystal whose concentration of phosphate is approximately 10% of the concentration of phosphate in the aqueous solution (e.g., a 5% phosphate solution gives crystals which contain ∿0.5% phosphate). In related experiments Pellett and Cofer (Reference 3) found that 6.8% of the phosphate in the original solution was coprecipitated with the AP.

b. AP Containing Chlorate

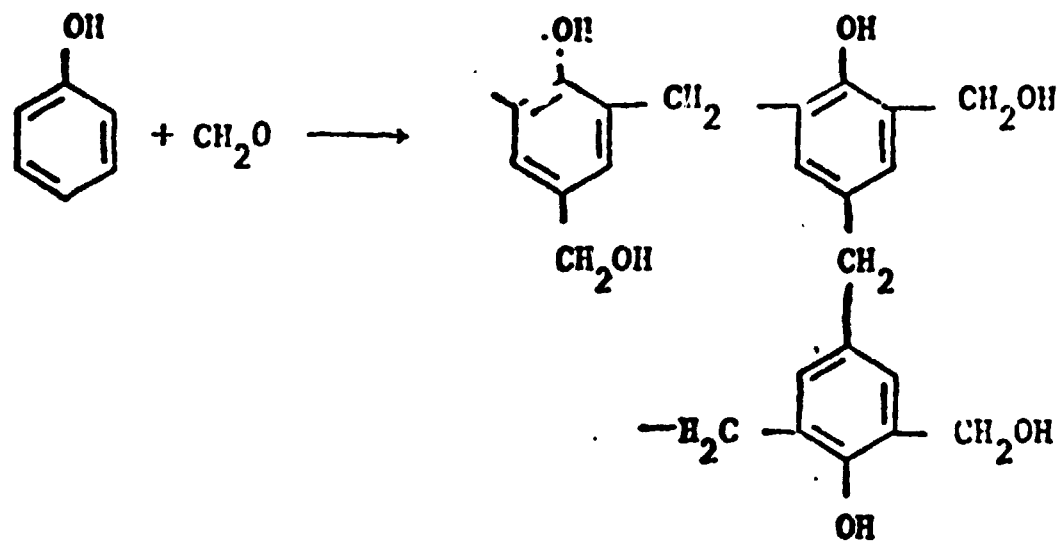
The required amount of AP is dissolved in water at ∿60°C. The desired amount of $KClO_3$ is then added and the solution taken to dryness under vacuum at ∿50°C. Chlorate is analyzed for by the method of Chen (Reference 4). This is a spectrophotometric method in which ferrous ion is used as a reducing agent. The quantity of ferric ion produced is measured in a sulfuric acid medium at 300mμ.

2. Phenolic Resins

A number of phenolic resins were prepared; however, only two of these were used in the combustion experiments. Both of these polymers, novalak and resole, are condensation polymers obtained from the reaction of phenol with formaldehyde.

a. Resole

Resole (Reference 5) was made with an excess of formaldehyde (1 mole phenol to 1.5 mole of HCHO). The extent of crosslinking depends on the preparative conditions, especially temperature. The material used in this program was only slightly crosslinked and contained hydroxymethyl groups which were available for further condensation, Reaction (1).

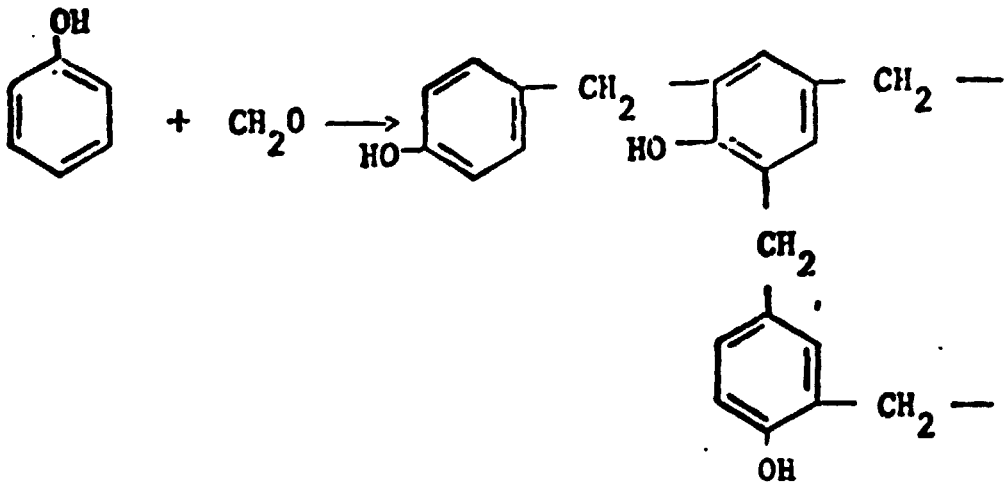


(1)

On further heating, the material becomes increasingly crosslinked and therefore less ductile.

b. Novalak

In this preparation (Reference 5), the phenol was in excess (1.4 mole phenol to 1.0 mole HCHO) of the formaldehyde, Reaction (2).



(2)

Novalak, unlike resole, contains very few hydroxymethyl groups and cannot condense further on heating.

3. Other Organic Fuels

The organic compounds, fuel components, listed in Table 1 were all reagent grade chemicals and were used as received from the manufacturer. The only treatment received by these materials was drying, either by temperature, vacuum or a combination of temperature and vacuum.

TABLE 1

PROPERTIES OF THE ORGANIC FUEL COMPONENTS

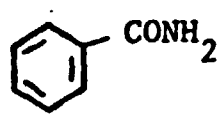
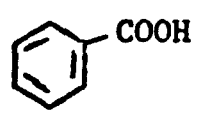
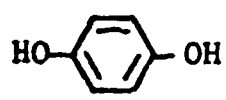
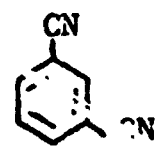
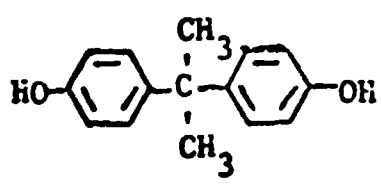
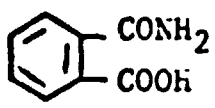
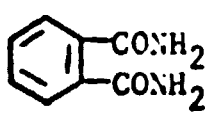
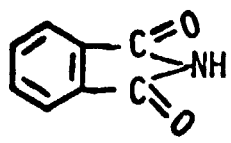
Compound		Melting Point °C	Boiling Point °C
Acetamide	CH_3CONH_2	69	222
Benzamide		130	290
Benzoic acid		122	249
Hydroquinone		171	286
Isophthalonitrile		161	s
4,4'Isopropylidenediphenol		157	~400
Paraformaldehyde	$(CH_2O)_n$	64	s

TABLE 1 (Cont.)

Compound		Melting Point °C	Boiling Point °C
Phthalamic acid		148	e
Phthalamide		220	d
Phthalimide		238	s
Starch	$(C_6H_{10}O_5)_x$	a	a
Stearic acid	$CH_3(CH_2)_{16}COOH$	70	383
Succinamide	$H_2C\text{-}CONH_2$ $H_2C\text{-}COHN_2$	240	d
Sucrose	$C_{12}H_{22}O_{11}$	160	a
Sucroseoctaacetate	$C_{28}H_{38}O_{19}$	83	~280

s = sublimes
d = decomposes
a = see Results Section

C. PRESSED AP STRANDS AND GRAINS

It was found experimentally that the forming pressure must be adjusted for each material or mixture of materials pressed. If the pressure is too low porosity results and if it is too high laminary fractures occur.

These conditions could not always be detected visually nor by density measurements. However, the pressure time trace obtained during combustion was a valuable tool in identifying these problems. We feel that this method of measurement allows us to detect and therefore correct problems that are not detectable when burning rates are measured by elapsed time between two wires. The general procedures and conditions used for pressing were as follows. The forming pressure was arrived at by trial, starting from a high pressure and decreasing the pressure on successive strands until a strand without laminary fractures was formed. This procedure produced strands as close to theoretically density as could be achieved by pressing. All strands were pressed at die temperatures of 40°C to 50°C. After pressing, the strands were sanded to remove any traces of die lubricant and then cut into segments which were coated with a polysulfide rubber for a restriction. Even ignition was achieved by a JPN disk which in turn was ignited by a hot wire. The burning rates were determined from pressure time traces and the length of the strands burned. Once the proper set of conditions was determined for a material or mixture, the use of the above procedures results in very reproducible results.

Basically the procedure for pressing the 38mm circular grains was the same as that used for the strands. However, the actual forming pressures were different in the two systems, for identical materials, due to differences in die wall friction. The pressed grain was attached to a phenolic plate which was then placed in the motor hardware. Ignition was achieved by hot gases sweeping across the face of the grain and the burning rate obtained from pressure time traces. These procedures have resulted in reproducible results.

II. RESULTS

The current year's effort is based on the framework of the previous year's conclusions (Reference 6) with the primary emphasis placed on the role of the fuel component in determining the combustion rate of AP-fuel composites. In addition, we have continued the investigation of the catalytic effect of both ClO_3^- ion and $H_2PO_4^-$ ion on the decomposition and combustion of AP. The decomposition of AP doped with these catalysts has been previously studied qualitatively (References 1 and 6).

A. ISOTHERMAL THERMOGRAVIMETRIC AP DECOMPOSITION EXPERIMENTS

In order to minimize the problem of self heating (inherent in studies of exothermic solid phase decomposition reactions) the sample was spread in essentially a mono particle layer on a thin sheet of glass wool suspended on an aluminum screen. The system was purged for ten minutes with nitrogen after which the gas was turned off and the decomposition allowed to take place under static conditions (no external gas flow).

It was found that the rate of decomposition is affected by the inert gas flow and the geometry of the sample container. Three different sample containers were tried under conditions of a slow flow of nitrogen gas. One configuration was that described above, the second was similar except that

instead of an aluminum mesh a solid piece of aluminum was used, and the third was an aluminum cup. The decomposition rates of chlorate doped AP samples, in the three different configurations, were as follows: mesh > solid plate > cup.

The isothermal studies, utilizing the thermogravimetric balance, were conducted over two temperature ranges, 200 to 235°C and 250 to 300°C. The majority of the experimental work was done in the temperature range of 250-300°C where AP has a cubic crystal structure. This range was selected so as not to be complicated by the crystal modification which occurs at ∿240°C or the increasingly high rate of sublimation at temperatures above 300°C. One particle size, 140μ (range 105-175μ), was used for all the decomposition experiments and the effect of varying particle size was not investigated. Twice recrystallized AP was used as a control for the positively catalyzed AP (containing ClO_3^-) and for the negatively catalyzed AP (containing $H_2PO_4^-$). In the latter case, two samples with different levels of $H_2PO_4^-$ were studied. The analyzed dopant level in these experiments was 0.025% for the chlorate doped AP and 0.011% and 0.052% for the phosphate doped AP.

The isothermal TGA experiments produced sigmoid shaped plots when the weight fraction decomposed was plotted against time for the four different samples investigated. Due to sublimation there is a continuing, although slower, weight loss after ∿30% of the original sample is consumed. These two regions were treated separately in fitting kinetic equations to the data.

The selection of a rate equation for the reduction of data from solid phase reactions is always somewhat arbitrary and involves essentially the best empirical fit to one of several probable equations. A contracting volume equation has been used by Jacobs (Reference 7) to analyze the sublimation of AP over the temperature range covered in this study. We used the same equation, $1-(1-\alpha)^{1/3} = kt$, to analyze the weight losses occurring after 30% of the sample was consumed by decomposition. Figure 1 is a typical rate plot of the four different samples at one temperature using the contracting cube equation. Although the samples varied considerably in the rate of their low temperature decomposition (discussed later), the rate at which the residue sublimed was essentially the same for all four samples. The rate data for sublimation at different temperatures are given in Table 2. These data fall on a single line, Figure 2, yielding the equation

$$\log (k/\text{min}^{-1}) = 7.84 - 28{,}850/4.576\ T$$

TABLE 2

RATE CONSTANTS FOR SUBLIMATION OF PRE-DECOMPOSED AP

Temperature °C	10^4 k min^{-1}(a) AP	0.011% Phosphate(b)	0.052% Phosphate(b)	0.025% Chlorate(b)
259 ± 2	1.00	1.03	0.95	0.97
268 ± 2	1.22	1.67	1.50	1.62
270 ± 2	1.57			
276 ± 2	2.67	2.30	2.27	2.33
286 ± 2	3.52	3.08	3.20	3.33
295 ± 2	5.72	5.32	5.17	5.45

(a) Based on contracting volume equation

(b) Level of dopant in AP

A preliminary examination of the data on the 'low temperature' decomposition indicated that the results from all four samples could not be fitted to the same kinetic equation. To reduce the data from that part of the weight loss curve corresponding primarily to decomposition, an equation was tried which is based on nucleus formation and growth. The data for pure AP and AP containing phosphate fit the Avrami-Erofeev equation, $[-\ln (1-\alpha)]^{1/n} = k(t-t_o)$, with $n = 2$ for $0.1 < \alpha < 0.9$. The same equation fits the data from the AP sample containing chlorate over a shorter range ($0.1 < \alpha < 0.5$).

It was noted that the maximum rate of decomposition for pure AP and AP containing phosphate occurred at $\alpha \sim 0.5$ while for AP containing chlorate the maximum rate occurred at $\alpha < 0.15$. Since the decomposition of the AP containing chlorate was deceleratory after the initial 10-15%, these data were more appropriately reduced by the unimolecular decay equation, $-\ln (1-\alpha) = kt$. The results fit this equation well from $\alpha = 0.1$ to $\alpha > 0.9$. In all of the data reduction the choice of a final weight loss to define where $\alpha = 1$ was subject to some error. From plots of weight loss against time, especially for the chlorate containing AP, it was possible to approximate the end of the decomposition reaction. In reducing the data from the chlorate containing AP, the best fit was obtained for $\alpha = 1$ defined at 30% and 31% of total sample weight. For consistency, all rates for this material were obtained using $\alpha = 1$ at 30% of total sample weight. The rates for pure AP and phosphate containing AP were obtained with $\alpha = 1$ at 33% of total decomposition.

Figure 3 is a typical plot of the low temperature decomposition rate data for AP and AP containing phosphate using the Avrami-Erofeev equation. The data were not corrected for the effect of sublimation as the rate of sublimation was from 10 to 25 times slower than that of the

decomposition reactions. Figure 4 is an Arrhenius plot of the decomposition rate data from 255°C to 300°C. Least mean square fits of the data for decomposition yield the equations,

$$\log (k/min^{-1}) = 5.06 - 18,990/4.576\ T$$

$$\log (k/min^{-1}) = 4.91 - 19,040/4.576\ T$$

and $$\log (k/min^{-1}) = 5.40 - 20,960/4.576\ T$$

for pure AP, AP containing 0.011% $H_2PO_4^-$, and AP containing 0.052% $H_2PO_4^-$, respectively.

Figure 5 shows two rate plots for the decomposition of AP containing 0.025% chlorate using the unimolecular decay equation. Since the rate of decomposition was ~200 times faster than the sublimation rate, the amount of sublimation during decomposition is negligible. It was not possible to construct a meaningful Arrhenius plot from the rate data obtained with the chlorate doped AP. Between 250 and 275°C the rate was almost independent of the temperature, however above 275°C the rate increased sharply with temperature, Table 3.

TABLE 3

RATE CONSTANTS FOR ISOTHERMAL DECOMPOSITION OF AP CONTAINING 0.025% ClO_3^-

Temperature, °C(a)	$10^2 k\ min^{-1}$(b)	% at which $\alpha = 1$
208	0.55	50
218	0.37	38
228	0.68	36
235	0.98	30
252	2.63	30
257	2.78	30
259	2.63	30
262	2.78	30
268	2.93	30
276	3.43	30
286	5.13	30
295	8.00	30

(a) °C ± 2

(b) Based on unimolecular decay rate equation

In the temperature range of 200 to 240°C the decomposition of only three materials, pure AP, 0.025% chlorate doped AP and 0.011% phosphate doped AP were studied. Due to the long times involved no attempt was made in these experiments to follow the sublimation reaction. A problem in reducing and interpretating the data obtained in this temperature range was that the percent of AP consumed in the low temperature decomposition was not the same at every temperature. With AP containing $H_2PO_4^-$ the reaction tended to level off close to 30-33% of total decomposition, however, with the recrystallized AP there was some variation, with the percentage decomposition increasing slightly with decreasing temperature. This variation was more pronounced with the AP containing chlorate ion, where the reaction consumed >50% of the total AP at the lower temperatures. Table 3 lists the kinetic data on the decomposition of the AP containing chlorate using the unimolecular decay reaction, $-\ln(1-\alpha) = kt$. The point at which $\alpha = 1$ was determined for each run and varied from 30 to 50% of the total AP. While the induction time decreased with increasing temperature, the decomposition rate was not a simple function of the temperature. The data from the AP and the phosphated AP were reduced again using the Avrami-Erofeev equation, $[-\ln(1-\alpha)]^{1/n} = k(t-t_o)$ with $n = 2$. A least mean square fit of these decomposition rate data, from 200 to 240°C, yield the equations

$$\log (k/\text{min}^{-1}) = 7.59 - 26{,}600/4.576\ T$$

$$\log (k/\text{min}^{-1}) = 5.16 - 18{,}400/4.576\ T$$

for pure AP and AP containing 0.011% phosphate respectively. Rate data obtained near the transition temperature, 240 ± 10°C, show a larger amount of scatter than data obtained above and below this transition and have not been included in the Arrhenius plots. While this procedure is somewhat arbitrary the decomposition of AP is complex enough without trying to include measurements on the material while it is undergoing a crystal transition. For pure AP the rate of decomposition below the phase transition temperature is relatively higher than that above this temperature with the rate at 235°C being approximately the same as the rate at 260°C.

B. COMBUSTION OF PRESSED OXIDIZER STRANDS

1. AP, Chlorate and Phosphate Doped AP

Recrystallized AP of a single particle size, $\overline{140}\mu$ (105-175μ), was used in all of these experiments. AP was doped and analyzed by the procedures listed in the experimental section. To determine the effect of positive and negative catalysis of the AP low temperature decomposition on combustion, the following materials, AP, AP (0.13% $H_2PO_4^-$), AP (0.64% $H_2PO_4^-$), and AP (0.1% ClO_3^-), were pressed and burned. Although both the chlorate and phosphate ions had a considerable effect on the low temperature decomposition rate of AP, as described earlier, they had only a limited effect on the

burning rate of a pressed AP strand. What effect they did exert on the burning rate appeared to be in the pressure region of 900 to 1500 psi. Although the reproducibility of burning rates was good for all four of these systems below 900 psi and above 1500 psi, there was a degree (±10%) of data scatter in the intermediate pressure region. The scatter was greater with the AP containing chlorate ion than with the pure AP, and the least with the AP containing phosphate. A plot of the data, Figure 6, for pure AP shows a change in the burning rate pressure exponent in the 900-1500 psi region. The results with the 0.1% chlorated AP, Figure 6, show a similar slope change but with data scatter over a larger pressure region than with pure AP. AP containing 0.13% $H_2PO_4^-$ had approximately the same burning rate, Figure 7, as did pure AP and the AP containing 0.1% ClO_3^- over the pressure range investigated. When the phosphate concentration was increased to 0.64%, there was a change in the burning rates and a reduction in the data scatter. At the low pressures, the 0.64% phosphated AP had approximately the same burning rate as the other samples; however, there was a smaller change in pressure exponent between the low and high pressure areas, Figure 7, than found with the other three samples. The largest difference in burning rates between pure AP and the AP containing 0.64% phosphate occurred in the intermediate pressure range of ∿1000 psi.

2. AP Catalyzed by $KMnO_4$

The decomposition and combustion of AP containing isomorphously substituted $KMnO_4$ has been previously studied. Recently Peterson (Reference 8) noted that the combustion of AP mechanically mixed with $KMnO_4$ was similar to that of AP cocrystallized with $KMnO_4$, that is, if the strand is not restricted it will not sustain combustion at any pressure up to 3000 psi (pressure limit of the experiments). The combustion of mechanical mixtures of these two materials has been further investigated in the current program. When AP (140μ) mechanically mixed with <62μ $KMnO_4$ (0.4 and 2.0 mole percent) was pressed into strands it would not burn without a restrictive coating. When a restriction was applied, sustained burning occurred but at a rate lower than that of pure AP, Figure 8. It was noted in qualitative experiments, at atmospheric pressure, that almost any form of a coating or shield, such as aluminum foil, would make it possible for the material to "burn", however, without this restriction, the composite would not sustain combustion. In the case where a restriction was used, at atmospheric pressure, there was no sign of a flame and the material decomposes in a condensed phase reaction. DTA traces of these mechanical mixtures are different from traces of AP isomorphously substituted with $KMnO_4$, Figure 9. The latter shows the start of an exothermic reaction prior to the AP phase transition temperature and depending on sample size and particle size, may deflagrate right at the phase transition temperature. The mechanical mixtures of these materials behave as most AP-catalyst mixtures do with decomposition occurring above ∿325°C.

3. Pressed Powder AP Grains

AP was pressed into 38mm diameter circular grains which were ∿12mm in depth. These samples were then tested as end burning motors. Due to the relatively low flame temperature of pure AP, compared to that of composites, and the fact that these grains were tested in existing hardware having a fairly large volume, the burning rate pressure traces were progressive. That is, it took a significant part of the burning time to get the motor up to the desired pressure. The AP grains were, therefore, tested under conditions in which nitrogen was used to obtain part of the desired pressure. In this testing configuration a ∿25% oversized nozzle was used and the motor obtained the desired pressure on ignition. Work has since been initiated on hardware whose configuration is such as to allow the end burning motor firing without supplemental pressure. The burning rates obtained using the supplemental nitrogen pressure method are shown in Figure 10. These burning rates agree well with those obtained with pure AP pressed strands that have been restricted with a polymeric resin. The only differences are at the lowest pressures where the motors burned somewhat slower than the strands. The interesting areas to note are the burning rates above 2000 psi where there is no indication of a negative pressure exponent and the rate at ∿225 psi. The latter pressure is below what is generally taken as the low pressure deflagration limit for AP at this temperature (26°C). However, it should be noted that there were signs of unstable burning at this lower pressure.

C. AP-FUEL DECOMPOSITION AND COMBUSTION STUDIES

There are a large number of data which show that the nature of the fuel component has a significant effect on the combustion rate of an AP composite propellant. General relationships between fuel properties and combustion rates have not yet been satisfactorily established. It was the aim of the current program to proceed experimentally in a manner such that the results would allow some generalization to be made about which properties of a fuel are important in influencing the combustion of a composite propellant. One of the most difficult experimental problems in this area is to isolate the variables. For example, changing the chemical composition of a fuel generally changes its physical properties (melting, etc.), similarly keeping a stoichiometric ratio between fuel and oxidizer may involve significant differences in the weight or volume of the various fuels needed.

For the majority of experiments the particl size of both the fuel and the oxidizer was held constant. The AP particle size selected was 140μ (range 105μ to 175μ) which is the same particle size used in all the other decomposition and combustion experiments. It was more difficult to screen the fuels to a given particle size. All fuels

were passed through a 62μ screen and caught on a 43μ screen. Often agglomeration more than particle size prevented much of the material from going through the 43μ screen. Therefore, unless otherwise noted the fuel particle size limits are given as <62μ. Experiments with several fuels showed no difference in burning rates between composites made with recrystallized AP and a specific lot of "as received" AP. Therefore, all the experimental combustion work with composites, in this program, was done with one lot of "as received" AP. For all systems investigated, the stoichiometry of the fuel-oxidizer mixture is based on the final fuel products being CO and H_2O.

1. Fuel Volatility

Two hydrocarbon fuels polyethylene (PE) and stearic acid (SA) were selected to determine the effect of fuel volatility on AP composite combustion. Polyethylene and stearic acid are both essentially saturated hydrocarbons (with the exception of the terminal COOH group on SA) which melt at a relatively low temperature, ≤100°C. They differ primarily in their volatility with the polymeric PE being relatively stable up to ∿400°C while stearic acid volatilizes (under our experimental conditions) by 300°C, Figure 11. While the temperature differential in their boiling points will decrease with increasing pressure, some differential will remain, especially at the lower pressures. Figure 12 compares the burning rates of pressed composites of AP-polyethylene (89.4/10.6) and AP-stearic acid (87.4/12.6). It can be seen that the burning rate of the PE composite is slightly lower at the lower pressures; however, due to a slightly higher pressure exponent it has approximately the same burning rate as the SA composite above ∿1000 psi.

2. Melting and Charring of Fuels

a. Sucrose, Sucrose Octaacetate and Starch

Sucrose, sucrose octaacetate, and starch were selected to study the effects of melting and charring on combustion. These three compounds make possible a comparison between a fuel which melts without charring, a fuel which melts with charring, and a fuel which chars without melting. While these compounds differ in these characteristics, they are similar in composition (carbon, hydrogen, and oxygen) and structure. TGA and DTA data, Figures 13 and 14, illustrate the thermal characteristics of these compounds. Sucrose octaacetate melts at 83°C and is relatively stable up to ∿280°C, after which point it volatilizes leaving no residue. Sucrose melts at ∿160°C, the melt then begins to boil and char between 210-240°C and is followed by gradual decomposition to a char residue of ∿30% at 400°C. The last of these compounds, starch, begins to char between 210-240°C without first going

through a melt. The char residue at 400°C is approximately the same as that for sucrose (∿30%). The charring temperature ranges and the amount of char residue are a function of such parameters as heating rate and must therefore be considered in conjunction with the experimental conditions under which they are obtained. While the experiments shown were performed under a nitrogen atmosphere, similar results were obtained in an oxygen atmosphere.

TGA experiments with mixtures of AP and these fuels indicated that, at least under the conditions of this experiment (sample is not confined and heat is relatively easily dissipated to the surroundings), the fuel and the oxidizer decomposed without interacting. The first step of the fuel decomposition is primarily a dehydration, however the percentage of char residue formed in these experiments indicated that some carbon was also lost. Figure 15 shows that in the AP fuel mixtures the fuel dehydration occurs before the AP decomposes. At the end of the reaction there was a char residue even in the presence of the AP.

The three materials were pressed in composites with AP to form mixtures containing 32.8%, 31.6%, and 29.28% sucrose, starch, and sucrose octaacetate, respectively. All materials were dried at 100°C for 24 hours before blending with the AP. It was not possible to get a cohesive strand with the starch-AP composite until ∿2.5% water had been added to the powder blend. The burning rates of these composites were measured at pressures of 100 to 3000 psi and these data are summarized in Figure 16. There are essentially no differences in burning rates between the starch and the sucrose composites, except a small variation at the highest pressures. The sucrose octaacetate, however, burned significantly lower at all pressures above 200 psi. It should also be noted the latter composite had a maximum in its pressure burning rate curve at ∿800 psi, fell to a minimum at ∿1800 psi, after which the burning rate increased up to the highest pressure tested, 3000 psi.

b. Phenolic Resins, Paraformaldehyde and Carbon

It was not possible to form a pressed strand with a composite containing a highly crosslinked phenolic-formaldehyde polymer, even if several percent water were introduced into the blend. To overcome this problem, two less crosslinked phenolic polymers, novalak and resole, were synthesized. Novalak is essentially a linear polymer with an excess of phenol which cannot polymerize further on heating while resole, which is made with an excess of formaldehyde, can crosslink further on heating. Resole used in this study was only slightly crosslinked and was still fusible. Whether additional crosslinking occurs in the actual combustion situation is not known. Both of these polymers thermally decompose so as to leave a residual char at temperatures up to 650°C (which was the highest temperature reached in the test),

Figure 17. The percentage residue indicates that in addition to dehydrogenation some of the carbon is lost (the residue found is ∿40% as compared to the carbon content of ∿70%). P-cresole (melting point ∿35°C) was initially selected as a fuel in this series as it is essentially a monomeric unit of the phenolformaldehyde polymer. However, it was difficult to handle, partially due to contamination by the lower melting ortho and meta isomers; thus a higher boiling compound was selected as the fuel for the control formulation. This is 4,4' isopropyidenediphenol (bisphenol A) which is similar to a dimeric unit of the phenolic resins. In addition to these three phenolic materials, paraformaldehyde and carbon black were selected as fuels in this series. The paraformaldehyde composites pressed easily while the carbon could not be pressed without the addition of ∿3% moisture.

Stoichiometry to give CO and H_2O as final products required the following fuel percentages; resole - 18.9%, novalak - 16.8%, bisphenol A - 15.6%, paraformaldehyde - 33.9%, and carbon - 17%. Figure 18 shows that near 400°C novalak reacted with AP and the material deflagrated. Similarly, the carbon AP mixture deflagrated at ∿400°C. In the mixtures of AP with the more volatile fuels, paraformaldehyde and bisphenol A, the fuel volatilized leaving the AP which then decomposed at essentially the same rate as pure AP, Figure 19. Figures 20 and 21 summarize the burning rate data obtained with these composites over the pressure range of 100 to 3000 psi. Comparing the composites made with resole and novalak with that containing bisphenol A, it is seen that the bisphenol A composite had a lower burning rate at all pressures. In this series there was less of a fuel component than in the sucrose series, yet the differences in burning rates between those composites whose fuel chars on decomposition and those which leave no residue are about the same in each series. In line with this, the composite with paraformaldehyde had a low burning rate compared to that with the non-volatile carbon. In the latter system, the particle size of the carbon is 2000 Å.

3. Chemical Reactivity

a. Benzoic Acid, Hydroquinone and Isophthalonitrile

Benzoic acid was taken for the basic formulation of this series of fuels. In addition to the comparisons within the series it is possible to make limited comparisons with aliphatic compounds such as stearic acid. Benzoic acid which is thermally more stable than stearic acid formed a composite with AP which had a lower burning rate, especially at pressures above ∿1000 psi, than the comparable stearic acid-AP composite (Figure 23 versus 12).

Since an area of interest in the combustion of AP composites has been the possibility of a fuel oxidizer reaction in the condensed phase or of gas-solid (or liquid) surface reactions, hydroquinone was compared to benzoic acid on the supposition that the

hydroquinone would be more reactive toward oxidizing species than would benzoic acid. This was borne out in DTA work with mixtures of AP and these fuels, Figure 22. The boiling points of these two compounds are very nearly the same, however, it can be seen that the hydroquinone caused a deflagration, in the DTA, at ∿380°C while the benzoic acid appeared to volatilize without interacting with the AP. The burning rates obtained with AP composites using these fuels were essentially the same over the pressure range studied (300-3000), Figure 23.

It is interesting to note that at pressures above ∿1000 psi the burning rates of the benzoic acid and hydroquinone composites were lower than those of AP without a fuel component. As part of both this and a later series, the burning rate of an AP composite with isophthalonitrile as the fuel was obtained. The burning rates of an AP composite with this fuel, which is thermally quite stable, are comparable with those of the hydroquinone and benzoic acid composites up to pressures of ∿2000 psi. Above 2000 psi there was a significant difference between the combustion rates of the nitrile composite and those of the other two aromatic fuel composites. The burning rate pressure exponent of the nitrile composite changed at ∿2000 psi above which pressure it is more positive than the other two formulations, Figure 25.

b. Triphenylmethane

It is difficult to fit this compound in any given category. While it is a substituted aliphatic hydrocarbon, the substituents are aromatic groups. The abstraction of a hydrogen from this compound will yield the relatively stable triphenylmethyl radical. If this radical were produced it would be expected to react at or near the point where it was formed. For example, if the radical was formed near the surface it would be expected to react further at that point rather than diffuse unreacted into the secondary flame. DTA shows that the fuel does react exothermally with AP below 400°C, however, the reaction does not consume the entire sample at that temperature (unlike the AP-hydroquinone reaction). The burning rates obtained with the composite containing triphenylmethane as a fuel exhibit an unusual pressure dependence. Figure 24 shows that the burning rate increased rapidly with increasing pressure up to ∿200 psi. From 200 to ∿550 psi the pressure exponent was essentially zero while above 550 psi there was again a positive pressure exponent which gradually decreased to zero at ∿2200 psi. The unique feature with this composite is the plateau in the region from 200 to 550 psi. This is the pressure region in which the fuel component may affect the burning rate but usually does not affect the pressure exponent.

c. Aluminum

Aluminum was chosen as a fuel which would not easily volatilize and therefore would either react at the surface or be ejected

into the gas phase. The aluminum used in these experiments was spherical and had a particle size range of 20 to 30μ. Burning rates were obtained with the AP-Al composite only between 800 and 3000 psi as it was not possible to achieve ignition below 800 psi with the normal igniter system, Figure 24. Using an extra large stand-off igniter it was possible to obtain ignition and burning at 600 psi. However, it was not possible to measure the burning rate in the latter case as the size of the igniter made it impossible to reduce the pressure trace data. At atmospheric pressure it was not possible to obtain ignition of the AP-Al composite even when using a gas oxygen flame from a glass blower's torch.

4. Fuels Producing NH_3 and/or H_2O

a. Benzamide and Acetamide

These compounds were selected on the basis that one of their decomposition products, ammonia or water, could affect the nature or rate of the AP combustion reaction. Acetamide can pyrolyze into three different sets of products.

$$CH_3CONH_2 \longrightarrow CH_2{=}C{=}O + NH_3 \qquad (1)$$

$$CH_3CONH_2 \longrightarrow CH_3CN + H_2O \qquad (2)$$

$$CH_3CONH_2 \longrightarrow HNCO + CH_4 \qquad (3)$$

Pyrolysis generally occurs by all three mechanisms. The path which produces the ketene and ammonia is optimized at ∿500°C which is close to the temperature generally accepted as the surface temperature of an AP composite propellant. There is no available data on how the relative contribution of the three paths vary with pressure. Benzamide is generally considered to decompose into the nitrile and water,

$$C_6H_5CONH_2 \longrightarrow C_6H_5CN + H_2O$$

however, a decomposition into an unstable aromatic and ammonia is possible.

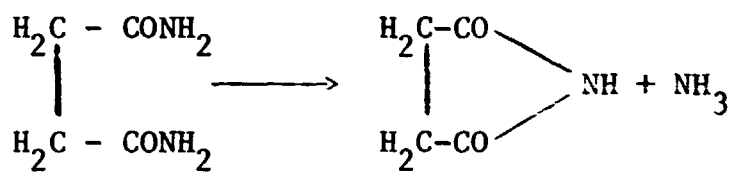
DTA studies with mixtures of AP and benzamide or acetamide showed that a reaction occurred at ∿350°C but that the sample was not consumed at this temperature, Figures 26 and 27. Final decomposition, at atmospheric pressure, does not occur until temperatures in excess of 450°C are reached. Mixtures of these materials with AP resulted in a slight increase in the DTA deflagration temperature of the mixture over that of pure AP (Reference 6) at 500 psi.

The combustion results obtained with composites utilizing these materials as fuel are quite interesting. The slope of the plot of log pressure vs log burning rate for the AP-benzamide composite is relatively flat between 200 and 2000 psi (burning rates of 0.19 and

0.27 inches/sec at 200 and 2000 psi, respectively). At 2000 psi there is a change in the pressure exponent with a relatively rapid increase in burning rate going from 2000 to 3000 psi, Figure 25. The low pressure exponent below 2000 psi was due not only to a depression in burning rate at the higher pressures but an increase in burning rate at the lower pressures. The combustion data from the AP-acetamide composite were less reproducible than those from the AP-benzamide composite. The burning of the AP acetamide can be qualitatively described as being very slow burning at atmospheric pressure, not sustaining burning between 200 and ∿600 psi, relatively slow burning between 600 and 2000 psi with a great deal of scatter in the data and exhibiting a rapid increase in burning rate above 2000 psi, Figure 25.

b. Succinamide

The mechanism for the thermal decomposition of succinamide, at least at atmospheric pressure, is less ambiguous than that for acetamide. The primary thermal decomposition path for succinamide yields succinimide and ammonia, (Reference 9).

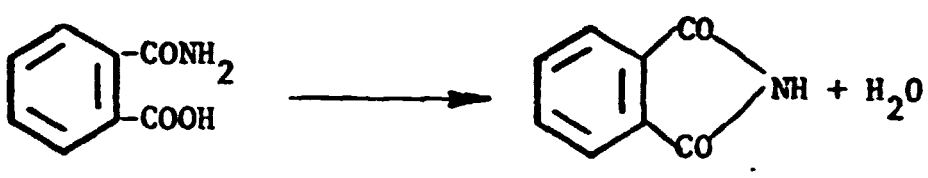


Succinamide does not reach a boiling point as it decomposes at its melting point to form the imide and ammonia, however, the succinimide does boil at ∿288°C. An atmospheric pressure DTA showed that the succinamide composite was not consumed, in the DTA, until the temperature gets above 450°C. At both atmospheric and elevated pressure a residual char was found at the end of the DTA run. Under combustion conditions it was not possible to obtain sustained burning with the AP-succinamide composite between 100 and 1500 psi. Even when extra booster igniters were used the composite either did not ignite or extinguished shortly after ignition. At atmospheric pressure it was possible to obtain burning although there was a tendency for the composite to extinguish. The burning rates at atmospheric pressure were between 0.01 and 0.02 inches/sec. Sustained combustion (using only the standard igniter) was obtained between 1500-3000 psi. At 1500 psi combustion was erratic and extinguishment occasionally occurs. The burning rates in the pressure range of 1500-3000 psi were between 0.05 and 0.07 inches/sec. This is approximately an order of magnitude slower than most composites and a factor of four slower than the next slowest burning composites. When 2% copper chromite (Cu 0202) was added to the succinamide composite the combustion results were drastically altered. Notably, combustion was sustained at all pressures tested and the burning rate was increased (over that of the uncatalyzed composite) by a factor of 2 or 3 at

the lowest pressures and a factor of ∿15 at the higher pressures. The pressure exponent was positive with a value of ∿0.6-0.7 between 300 and 3000 psi, Figure 28.

c. Phthalamide and Phthalamic Acid

Phthalamide decomposes by a mechanism which is similar to that of the thermal decomposition of succinamide to form phthalimide and ammonia. The thermal decomposition mechanism of phthalamic acid is similar to that of the diamides with the primary difference being that H_2O rather than NH_3 is formed alorg with the imide.



As with the succinamide the decomposition to the imide plus NH_3 or H_2O begins at the melting point temperature of these compounds, however, unlike the succinimide product the phthalimide formed can further decompose (starting at ∿350°C) for form the thermally stable nitrile, (Reference 10).

The combustion results from the AP-phthalamic acid composite were very similar to those obtained with the AP-benzamide composite. With the phthalamic acid composite the pressure exponent was essentially zero from 300 to 1500 psi above which pressure the exponent was ∿0.9. In the region of pressure independence the burning rates were ∿30% lower than those obtained with the benzamide composite, Figure 29. The burning rates obtained with the AP-phthalamide composite were again relatively low, however, the pressure exponent was unique for this series. The pressure exponent was positive between 150 and 800 psi above which it became negative such that the burning rates at 1500 and 250 psi were approximately equal, Figure 29. It was not possible (for reasons yet undetermined) to obtain burning rates between 1500 and 3000 psi with this formulation (there were many cases in which the composite failed to ignite and a few in which ignition occurred but was immediately followed by a pressure surge).

C. REACTIONS OF FUELS AND CATALYSTS WITH PERCHLORATE ION

It has been reported that potassium perchlorate (KP) does not decompose between 300-400°C, while KP pressed with carbon does decompose in this temperature range at an appreciable rate (Reference 11). This suggests the possibility of a direct perchlorate ion-fuel reaction. A similar experiment was tried in this program with KP and polyethylene (PE). Thermogravimetric results show that PE is relatively stable up to ∿400°C. Since PE melts at ∿100°C, good physical contact is established between the PE and KP; however, as the DTA in Figure 30 shows, there was no obvious interaction between these two materials. This was confirmed by isothermal TGA runs at ∿400°C. From a comparison of these two fuels (carbon and PE) it is concluded that not only must the reaction between an oxidizer, such as KP, and a fuel be thermodynamically feasible it must proceed at a reasonable kinetic rate. To further investigate this line of reasoning, some 'fuels' which have the thermodynamic potential to reduce perchlorate ion were tested. These include the following salts, KCN, KSCN, KCNO, and $K_2S_2O_3$. Some redox potentials for the anions of these salts are:

$CNS^- \longrightarrow$	$1/2\ (CNS)_2$	-0.77
$S_2O_3^= \longrightarrow$	SO_3	-0.40
$HCN \longrightarrow$	C_2N_2	-0.37
$C_2N_2 \longrightarrow$	HCNO	-0.33

The exotherms noted in Figures 31 and 32 show that all four compounds reacted with $KClO_4$, this despite the fact that KCN and KCNO do not melt or decompose at temperatures <600°C. The reaction which occurred at the lowest temperature and was the most vigorous is that between $KClO_4$ and KSCN (which melts at 173°C). The reaction was strongly exothermic, actually detonating immediately above the phase transition temperature (300°C) of $KClO_4$. All four of the reducing agents reacted exothermically with $KClO_4$ by ∿400°C and the reaction with KCN as with KSCN resulted in a detonation.

In a general survey of all the compounds containing transition elements that have been used as combustion catalysts, only those containing copper or iron have had any appreciable effect on the burning rate. On the supposition that a possible step in the catalyzed decomposition of AP is the reduction of ClO_4^- or $HClO_4$, a survey was made of the oxidation-reduction potentials of metal systems relative to the potential of the chlorate-perchlorate couple. Although the potentials used are for reactions in solution, they are useful for comparison purposes. It is immediately striking that the oxidizing member of the following redox couples are all thermodynamically stronger oxidizing agents (in the specific reactions listed) than perchlorate ion or perchloric acid. The E° redox values are for acid conditions, (Reference 12).

$Co^{2+} \longrightarrow$	Co^{3+}	+ e	-1.8
$MnO_2 \longrightarrow$	MnO_4^-	+ 3e	-1.7
$Ce^{+3} \longrightarrow$	Ce^{+4}	+ e	-1.6
$Mn^{+2} \longrightarrow$	MnO_4^-	+ 5e	-1.5
$Mn^{+2} \longrightarrow$	Mn^{+3}	+ e	-1.5
$Pb^{+2} \longrightarrow$	PbO_2	+ 2e	-1.46
$Cr^{+3} \longrightarrow$	$1/2\ Cr_2O_7^{-2}$	+ 3e	-1.3
$Tl^{+} \longrightarrow$	Tl^{+3}	+ 2e	-1.25
$Mn^{+2} \longrightarrow$	MnO_2	+ 2e	-1.23
$ClO_3 \longrightarrow$	ClO_4	+ 2e	-1.19

This list contains transition metals which have been tried as AP composite combustion catalysts with little success. Notable in this group are Mn^{+2} salts, MnO_2, Co^{2+}, and Cr^{3+} salts. On the other hand, perchlorate is a better oxidizing agent than the oxidizing member of the following couples.

$Fe^{2+} \longrightarrow$	Fe^{3+}	+ e	-0.77
$Cu \longrightarrow$	Cu^{+}	+ e	-0.52
$Cu^{+} \longrightarrow$	Cu^{2+}	+ e	-0.15

The salts of these metals have proved to be good combustion catalysts.

In experiments to determine if the redox reaction being studied involves ClO_4^- rather than the decomposition of perchloric acid, $KClO_4$ was used as the oxidizer. Figure 33 shows the difference in effect of the two valence states of copper (Cu^{+1} and Cu^{+2}) on the reaction of their oxides with $KClO_4$. If the $KClO_4$-Cu_2O mixture is reacted in the presence of an organic fuel, the decomposition of $KClO_4$ goes to completion.

III. DISCUSSION

AP Decomposition and Sublimation - There have been two mechanisms proposed to explain the uncatalyzed decomposition of AP between 200 and 300°C. One is an electron transfer process the other a proton transfer process. Most of the evidence to date supports the idea that the decomposition of AP in this temperature range involves a step in which $HClO_4$ is formed by means of a proton transfer. In a recent paper

(Reference 7), a reaction scheme is presented in which a proton transfer occurs forming NH_3 and $HClO_4$ adsorbed to the crystal. These species then diffuse over the surface and either desorb (sublimation) or react (decomposition). It has been argued that decomposition occurs or at least is initiated on the surface of the crystal, and that the first step in the decomposition may be the bimolecular reaction of $HClO_4$. The latter possibility has also been suggested by Wise (Reference 13) in an earlier investigation. The present work adds experimental evidence to this basic scheme and also extends the concepts to help explain the differences in rates of decomposition determined by different investigators.

When the concentration of NH_3 in the atmosphere surrounding the sample is sufficiently high neither decomposition or sublimation of AP occurs between 200 and 300°C (Reference 1). These results support a reaction scheme which has as one step in the mechanism an equilibrium between AP and its dissociation products NH_3 and $HClO_4$, Equation 1.

$$NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4 \qquad \text{Eq. 1}$$

That the decomposition reaction takes place primarily on the crystal surface is supported by the results from the hot plate experiments with physical mixtures of AP and Na_3PO_4 which show that the AP decomposition is affected not only when the phosphate is cocrystallized with the AP but also when it is mechanically mixed with the AP (Reference 6). The data from Reference 6 suggest that once $HClO_4$ is formed on the surface of the crystal it can either desorb or by some mechanism decompose. In the presence of the phosphate there is a shift in the relative contributions of these two paths toward an increase in desorption relative to decomposition at temperatures between 330 and 378°C. Whether the former path is aided or the latter retarded is not clear from these experiments. However, the current isothermal decomposition experiments indicate that the sublimation rate is unaffected (discussed below) while the decomposition mechanism is retarded by the phosphate salt.

By following the sublimation process after the low temperature decomposition it was found that the sublimation rate is essentially unaffected by residual additives which had perturbed the rate of low temperature decomposition; i.e., the residues from AP containing chlorate and from AP containing phosphate sublime at the same rate. This indicates that the residue in all cases was physiochemically similar and that the remaining impurities, e.g., $H_2PO_4^-$, do not affect the sublimation process at least in the temperature range of 259-295°C. The rate equation used to reduce the weight loss data is based on the idea of a 'contracting cube'. Since the sublimation process involves desorption of molecules from the surface of crystals this model appears to at least approximate the process. The rate equation obtained from these data is almost identical to that obtained by Jacobs (Reference 7)

over this temperature range and for α up to $\sim$0.5. Later work by Jakobs (Reference 14) and a discussion of this work by Williams (Reference 15) suggests that at higher temperatures and if the reaction is followed further than α = .5, the contracting cube equation is inadequate.

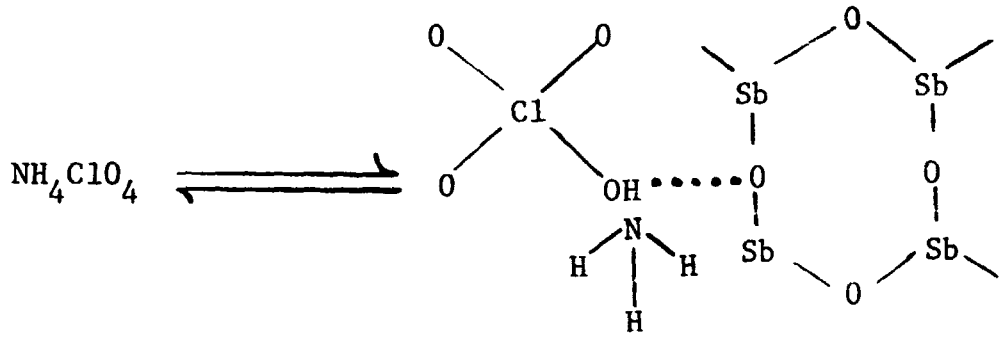
It is important to remember that the actual measured rate is sensitive to the conditions of measurement and that the rate determining step may well vary depending on the experimental condition. The most likely mechanism involves an initial equilibrium, Eq. 1, followed by surface migration and then desorption. The relative approach to equilibrium achieved between adsorbed and gas phase molecules of NH_3 and $HClO_4$ is controversial and probably varies with experimental conditions. The gas phase concentration of NH_3 and $HClO_4$, adjacent to the surface, in turn is a function of their diffusion coefficient and such external parameters as inert gas flow and rate of their recombination which can be influenced for example by the insertion of a cold finger. As an example of how the process can be influenced by experimental conditions, the rate of sample consumption is much faster in the hot plate experiments than in the isothermal TGA experiments. In the former case the overall reaction is driven forward by condensing the sublimate rapidly immediately above the sample surface. The observed rate expression as well as the derived activation energy for sublimation therefore may include several equilibrium constants and without knowing these it is difficult to say anything about the rate of a specific reaction.

If the proton transfer were rate determining, rather than an equilibrium, factors affecting the removal of gaseous species should not affect the observed rate. Since these external factors do affect the rate, the determining step may involve either the desorption of NH or $HClO_4$ from the surface or their diffusion away from the surface. If for example, both species desorb with equal facility, then diffusion may be rate controlling. In this case NH_3 may be expected to diffuse more rapidly than $HClO_4$ making the diffusion of the latter the rate determining step. Recognizing these limitations on the meaning of the observed rate of weight loss, our results shown in Table 2 characterize the dissociative evaporation process for granular AP over the temperature range of 250-300°C at one atmosphere pressure with no external gas flow. The Arrhenius plot of the rate constants for these four samples shows that within the accuracy of our measurements, not only the dissociative evaporation rate at a given temperature but the change of rate with temperature is independent of the rate of the earlier low temperature decomposition.

Over the temperature range of 200-300°C an NH_3 atmosphere can stop the AP decomposition at any point in the decomposition reaction (Reference 1). This effect of NH_3 on the reaction suggests there is an equilibrium step in the decomposition mechanism in which NH_3 is one of the equilibrium species. This equilibrium must either occur before the rate determining steps or it must be the rate determining step. In addition, the negative catalysis by basic additives such as phosphate, antimony or arsenic oxides, especially when mechanically mixed with the

AP, suggests an interference with a process occurring on the surface of the crystal. These two observations are in keeping with the hypothesis of a proton transfer reaction, Eq. 1, followed by surface migration of the $HClO_4$ molecules. If decomposition results from a bimolecular perchloric acid reaction and this is the rate determining step the observed rate would be a function of the $HClO_4$ concentration. Since the sublimation data indicate that the phosphate has little effect on the rate of dissociative evaporation it appears that the basic additive affects decomposition by interfering with surface diffusion rather than by repressing the proton transfer equilibrium. If this is a correct interpretation then conversely surface diffusion is not necessary for dissociative evaporation, or it is fast compared to the rate determining step. These latter conclusions are based on sublimation data obtained with pre-decomposed AP and may not be valid during the time that the AP is still decomposing.

The chemical properties of the effective negative catalysts such as Sb_2O_3 suggests that the slowing down of surface diffusion may be due to some form of hydrogen bonding, Eq. 2.



(2)

An alternate mechanism which is mechanistically similar, and which is compatible with the data, would invoke the occurrence of proton transfer over the entire surface rather than actually having a mobile $HClO_4$ molecule. Another possible mechanism would be the unimolecular decomposition of the $HClO_4$ molecule with the additive stabilizing the decomposition by effecting the stability of the HO-Cl bond through some form of hydrogen bond. Neither the measured rate of homogeneous $HClO_4$ decomposition or the temperature dependence of the rate (Reference 16) are compatible with the data from this study.

A reaction mechanism for AP decomposition between 200-300°C is proposed which involves proton transfer to form $HClO_4$. The $HClO_4$ then diffuses over the surface until it reacts with a second $HClO_4$ molecule after which the products of this reaction, at least partially, oxidize the ammonia on the surface. This can be represented as follows,

$$NH_4ClO_4 \underset{}{\overset{K}{\rightleftharpoons}} NH_3 + HClO_4 \quad (a)$$

$$HClO_4{}_{(a)} \xrightarrow{k_d} HClO_4{}_{(b)} \qquad (3)$$

$$2\ (HClO_4)_{(b)} \xrightarrow{k} \text{Products} \qquad (4)$$

where (a) and (b) refer to different crystal sites and all molecules involved in the reaction are on the crystal surface. The observed rate (weight loss) can then be described by

$$k_{obs} = k\ (HClO_4)^2 \tag{5}$$

or

$$k_{obs} = k\ \left(\frac{K}{NH_3}\right)^2 \tag{6}$$

The concentration term also includes the rate of surface diffusion. Decreasing the rate of diffusion is effectively the same as decreasing the concentration of $HClO_4$ available for reaction. The observed diffusion constant is related to the true diffusion constant by a relationship which involves the concentration of the basic additive such as Eq. 7,

$$k_{d(obs)} = \frac{k_d}{[B]^n} \tag{7}$$

where [B] is the concentration of the basic additive.

Recent work has shown that decomposition propagates by repeatedly establishing nucleation sites which then grow and that the final extent of growth of all the nuclei are approximately the same (Reference 17). If propagation initially occurs essentially through the establishment of nuclei rather than the growth of these nucleation sites, the initial rate of decomposition may be represented by the rate of establishment of nucleation sites. These sites could result from the bimolecular $HClO_4$ reaction. The induction period is the time during which the concentration of $HClO_4$ on the surface is being built up and is followed by a relatively rapid formation of nuclei. As the amount of undecomposed AP available for nucleation decreases the rate of formation of new nuclei decreases and the overall reaction becomes deceleratary.

It is obvious that the choice of the rate equation used in reducing the kinetic data from the isothermal weight loss experiments is somewhat arbitrary. The Avrami-Erofeev equation, with n = 2 was used to reduce the data for the decomposition of both the AP and the phosphate doped AP samples. The justification for using this equation is that it is based on a model of nucleus formation and growth and that the data fit this equation over a wider range than they fit other equations such as the Prout-Tompkins. The decomposition rates determined in this study using the Avrami-Erofeev equation are much slower for dispersed granular AP (~26 times) than the rates obtained by Jacobs (Reference 7) for the same process, with compressed pellets of AP, using the same equation. These rates are not directly comparable to those of many other workers since a wide variety of kinetic expressions have been used to derive rates. In some earlier work a variation was noted in results between

pressed pellets and powder AP (Reference 18) and Bircumshaw (Reference 19) qualitatively noted a faster rate of decomposition if the AP was in a mound as opposed to the same sample size being spread over a larger surface. Rate constants from the present study compare, within a factor of 2, to those obtained by Bircumshaw. Since self heating is inherent in exothermic AP decomposition, it is to be expected that there would be variations in the rate due to non-isothermal conditions in the sample, especially in compressed pellets.

If one examines the work of other investigators on the decomposition of AP in the cubic modification, it is found that most of the activation energies reported are in the region of 17-22 Kcal (References 13, 19, 20, 21). In Jacobs later work (Reference 7), his value for the activation energy for this temperature region has been revised down to 26 Kcal. Self heating of the sample is a relatively greater problem at the higher temperatures which can lead to apparent activation energies that are higher than if the sample temperature had approached isothermal conditions.

The value found in this study for the activation energies for the AP samples containing phosphate were approximately the same as that for pure AP, between 250-300°C. The slightly higher value for the samples containing 0.052% phosphate may be due to having neglected the rate of sublimation in the calculations (the sublimation rate increases faster with temperature than does the decomposition rate). In the case of the relatively slowly decomposing AP/0.05% $H_2PO_4^-$ (rate of sublimation ~1/10 rate of decomposition), neglecting sublimation could give an apparent rate that is somewhat faster than the real decomposition rate at the higher temperatures.

For both AP and AP containing phosphate there is a discontinuity in the Arrhenius plot in the region of the AP phase transition temperature. The AP decomposition rates below the phase transition are relatively higher than those just above this temperature. This discontinuity is very similar to that observed by Bircumshaw with the rate at 235°C being approximately the same as the rate at 260°C for pure AP. For this reason data between 230 and 250°C were not used in figuring activation energies and frequency factors. The rate data for AP decomposition between 200 and 230°C are not as reproducible as those obtained above the phase transition temperature. In the lower temperature range the percentage of AP consumed in the decomposition reaction is not the same at every temperature. With AP containing $H_2PO_4^-$ the reaction tends to level off close to 30-33% of total decomposition. With recrystallized AP there is some variation, with the percentage decomposition generally increasing with decreasing temperature. This variation is even more pronounced with the chlorate doped AP, with the reaction consuming up to >50% of the total AP at temperatures around 200°C. The AP and the phosphated AP decomposition data, at these lower temperatures, were again reduced using the Avrami-Erofeev equation, with n = 2. Unlike

the decomposition of AP when it is in the cubic crystal modification the activation energy for decomposition of the recrystallized AP and the phosphate doped AP are not the same when the AP is in the orthorhombic crystal form. The reason for this is not clear. It is possible that the diffusion rate on the surface of the single orthorhomibic crystal is significantly different from that in the cubic modification where the original crystal has been broken down into smaller crystallites. They may then result in a change in the relative contribution of the surface diffusion term to the observed rate in pure AP and phosphate doped AP. Considering the small temperature range covered and the variability of α with temperature it would be unwise to make too much of an interpretation on an activation energy change of 6 or 7 Kcal.

The effect of ClO_3^- ion on the decomposition of AP can be explained within the same framework suggested for AP and AP containing phosphate. It has previously been shown that the decomposition of NH_4ClO_3 can be retarded by NH_3 (Reference 22), and the current study has demonstrated that the decomposition of AP containing ClO_3^- is also repressed by an NH_3 atmosphere. This suggests that the reactive species may not be the ClO_3^- ion but rather $HClO_3$, formed by NH_4ClO_3 dissociation, and that nucleation may result from the bimolecular reaction of $HClO_4$ and $HClO_3$. The rate constant for the reaction of $HClO_3$ with $HClO_4$ may be considerably faster than the rate constant for the bimolecular reaction of perchloric acid. An alternate explanation is that the $HClO_3$ directly oxidizes NH_3 forming a nucleation site. The maximum rate during the decomposition of AP and AP containing phosphate occurred at $\alpha \sim 0.5$ while for AP containing chlorate the maximum rate occurred at $\alpha \sim 0.1$. This suggested that for AP containing chlorate the unimolecular decay equation rather than the Avrami-Erofeev equation may provide the best fit for the data. The data do in fact fit the unimolecular decay equation well from $\alpha = 0.1$ to $\alpha > 0.9$. The rates derived from this kinetic expression when plotted against the inverse of the temperature, at temperatures between 250-300°C, do not give a straight line over the entire temperature range. In the region from ~250°C to 270°C, the slope is essentially zero. At temperatures >270°C, the rate constants increased at an accelerating rate. Below 235°C the unimolecular decay equation is again appropriate however, the point at which $\alpha = 1$ had to be defined for each run and varied from 30 to 50% of the total AP. It can be seen that at the lower temperatures, once decomposition begins, the decomposition rate is relatively independent of temperature.

If the decomposition proceeds by establishing nucleation sites the ease of formation and the amount of these sites would be expected to affect the general shape of the decomposition curve. The decrease in induction time, with AP containing chlorate ions, could be due to the lower concentration of $HClO_4$ necessary for reaction to occur with the $HClO_3$. Additionally if the reaction between $HClO_4$ and $HClO_3$

proceeds relatively rapidly a great many nucleation sites will be formed early in the decomposition leading to the generally deceleratary nature of the decomposition curve. When Eq. 5 is replaced with Eq. 8

$$k_{obs} = k_1 (HClO_4)(HClO_3) \qquad (8)$$

it can be seen why the rate of decomposition is a function of $HClO_3$ concentration. The lesser effect of phosphate on the AP decomposition rate when both phosphate and chlorate are present (Reference 3), can also be understood in terms of Eqs. 5 and 8. In the reaction with $HClO_3$ the rate is proportional to the $HClO_4$ concentration while in the bimolecular reaction, Eq. 5, the rate is proportional to the square of the $HClO_4$ concentration. The small temperature dependence for the rate of weight loss once decomposition begins suggests that there is either a very small activation energy for the reaction of $HClO_3$ with $HClO_4$ or that nucleation is essentially complete in the early stages of decomposition and what is being observed is the growth of the nucleation sites. The rate determining step in the mechanism of nucleation sites growth may have a low temperature dependence. It should be noted here that while phosphate decreases the overall decomposition reaction by a factor of ∿2 the equivalent amount of chlorate increases the rate by an order of magnitude. The reason for the rapid increase in chlorated AP decomposition rates at temperatures above ∿270°C is not clear. In this region, based on DTA experiments, self heating from the exothermic decomposition can be a problem; however, since the reaction appears to have essentially a zero activation energy between 250 and 270°C, a temperature increase should not appreciably affect the rate. Even in this area of essentially temperature independent reaction rates (AP containing chlorate), there is a discontinuity at the phase transition with the rates above the transition ∿4 times as fast as those below the phase transition temperature.

AP Combustion - The combustion of AP, either in pressed strands or single crystals, has been studied by a large number of investigators. The burning rate as a function of pressure, especially at pressures above 2000 psi, has been found to be strongly affected by whether or not the strand was restricted by an 'inert' material. In this study, all of the strands were restricted with a thin layer of polysulfide. The burning rate of pure AP as a function of pressure was essentially the same as that found by other investigators over the range of 300-2000 psia. Our results, in line with those of other investigators who restricted their strands, did not show the negative pressure exponent between 2000-3000 psi found by investigators using unrestricted strands or single crystals.

Glaskova (Reference 23) showed that increasing the size of the AP pellet did not eliminate the negative pressure exponent but did shift it to higher pressures. We extended this approach, making what could be described as an end burning motor, by pressing AP into a disc 38mm in diameter. Burning rates obtained with these large unrestricted discs

were essentially identical to those obtained with restricted AP strands, i.e., there was no negative pressure exponent, at least below 3000 psi. These motor results are significant because the experimental conditions eliminated the question of whether the polymeric restriction also serves as a fuel.

It appears that the negative slope found above 2000 psi is an artifact of the strand size. In fact, Friedman (Reference 24) has shown earlier that if the strand is small enough $\leq$ 4mm, it will not burn at any pressure. An explanation for the observed burning rates of AP between 2000 and 4000 psi may be found in the observations of Boggs (Reference 25). The sequence of events he described from his high speed movie studies of AP combustion over this pressure range is: (1) a portion of the surface is heated, (2) flame spreads to heated area, (3) enhanced regression rate ensues due to flame, (4) flame heats adjacent areas, and (5) the cycle repeats. If the flame spread is, as Boggs suggests, dependent on the heating of an adjacent area the perimeter to area ratio would be important. Thus, in the very small samples <4mm self deflagration is not sustained while in the large diameter (38mm) samples, the burning rate has a small positive pressure exponent between 1000 and 3000 psi. The size of most of the other samples, so far tested and reported in the literature, have been closer to the 4mm than the 38mm size and have negative pressure exponents over this pressure range. Similarly if a restriction is used it would be expected to affect flame spreading at the edges of the strand and thereby influence the combustion rate. At the lower pressures it is interesting to note the large AP grain has lowered the low pressure deflagration limit of AP below that found with smaller strands. However, there is still evidence that a low pressure deflagration limit exists, as can be seen by the somewhat erratic (pulsating) burning obtained at 225 psi with the 38mm AP grain.

The pure AP pressed strand data are not greatly altered when AP containing chlorate or phosphate is used even though these materials have a significant effect on the AP decomposition reaction. Based on earlier work (Reference 6) this is not an unexpected result. It has been shown that the 'low temperature' decomposition has little effect on the burning rate and both of these additives affect the 'low' but not the 'high' temperature decomposition. There does, however, appear to be a small effect of these materials on combustion. The cocrystallized phosphate (0.13 and 0.64%) and chlorate (0.10%) had: (1) variable but significant retarding and accelerating effects (about -6%, -18% and +3%, respectively) on the burning rates of pressed AP strands over the range 900-1500 psi, and (2) somewhat smaller burning rate effects (about -5%, -12%, and +2%, respectively) over the range 350-900 psi. Some data scatter was found in the pressure range of 900-1200 psi.

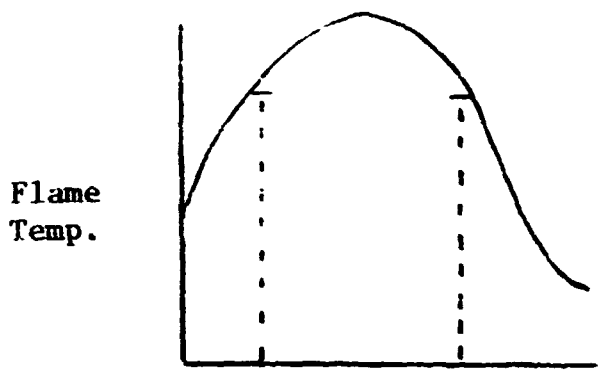
The scatter in the burning rate data is greater for strands of AP that are doped with chlorate than it is for pure AP strands. The best burning rate reproducibility was obtained with strands of phosphate doped AP, especially at the higher phosphate concentration. It is in the pressure region, where the data scatter occurs, that the burning rate pressure exponent of pure AP changes and that the deflagrating AP goes from a melt to a 'dry' surface condition (Reference 25).

The DTA's of mechanical mixtures of AP and $KMnO_4$ and $KMnO_4$ isomorphously substituted in AP are significantly However, in the combustion situation the two systems exhibit the same general characteristics. In both cases the difference between restricted and unrestricted strands is dramatic with the unrestricted strand not sustaining combustion at any pressure up to 3000 psi at concentrations of $KMnO_4$ as low as 0.4 mole percent. It is interesting that in the case of the $KMnO_4$ catalyzed restricted strand the burning rate is lower than that of pure AP even though the $KMnO_4$ lowers the deflagration temperature (as measured by DTA) of AP to $\sim$200°C. Since earlier work has shown the decomposition of this material is insensitive to an NH_3 atmosphere it appears that the material decomposes by a mechanism which is different from that of pure AP. This is supported by mass spectrometry results which show little evidence of $HClO_4$ and NH_3 getting into the gas phase (Reference 26). These data in conjunction with the visual observation of the atmospheric "burning" of a pressed strand of this mixture suggests that a large amount of the decomposition occurs in the condensed phase. The lower burning rates obtained with the mixture of AP and $KMnO_4$ may be the result of a much lower flame, and therefore, surface, temperature due to the change in the combustion mechanism of AP in the presence of $KMnO_4$. The fact that combustion is sustained only when the strands are restricted indicates that net heat balance at the surface is critical in the self deflagration of this composite. What is surprising is that $KMnO_4$ has the same effect on combustion whether it is mechanically mixed with or isomorphously substituted in the AP.

Combustion of AP-Fuel Composites - It may be useful to start with a general discussion of AP-composite burning rates. The pressure exponent of the burning rate has generally been associated with gas phase reactions and/or a diffusion mechanism (Reference 27). For the sake of discussion, let us assume that a single condensed phase or surface reaction is rate controlling in the burning process. It is not necessary that any significant amount of heat be released in the condensed phase; in fact, the overall reaction at this point may be endothermic. If this hypothetical reaction has a rational frequency factor and say an activation energy between 20-50 Kcal/mole, it can be easily seen that a 10-20°C temperature change would change the burning rate by a factor of 2 or 3. This magnitude of temperature change is within the error limits of all the direct means of surface temperature measurement so far attempted. An examination of AP and AP-composite burning rates between 300 and 1000 psi shows that the increase in burning rate over this range is

~2 or 3. If a single condensed phase or heterogeneous reaction is rate controlling it is not unreasonable to expect the burning rate to be affected by the surface temperature of the propellant, which in turn is a function of the heat balance at the surface.

The surface temperature is a function of several variables, the two which we are interested in being, flame temperature and the surface 'chemistry'. A representative plot of flame temperature against percent fuel in an AP-composite is depicted below.



If the flame temperature were the only important parameter, composites formulated at a and b should have identical burning rates. A typical plot of burning rate against fuel usually shows that formulations a and b do not have the same burning rates (Reference 28). It can be seen that while on the oxidizer rich side of stoichiometry there is some correlation between flame temperature and burning rate, on the fuel rich side this relationship does not exist. It is on the fuel rich side that practical composite propellants are formulated and it is in this area that the study of the effect of fuel on combustion can be expected to be the most fruitful.

The second consideration in determining the heat 'balance' at the surface is the summation of all the chemical reactions occurring at or immediately adjacent to the surface. Initially, if it is assumed that the oxidizer and fuel do not interact at this point, then the net heat at the surface is simply the heat flux from the flame minus heat losses to the substrate and surroundings, $\pm$ the sum of the heat of decomposition and vaporization of the fuel and oxidizer. Most calculations, such as I_s are concerned with the total combustion of the system; however, for the present arguments, what is important is the net heat of all reactions right at the surface. For example, a fuel that is totally vaporized before reacting further up in the flame may consume more heat and therefore cause a 'cooler' surface condition than a fuel which is dehydrogenated at the surface. While the flame temperature for both of these composites may be the same, the net heat balance at the surface will be quite different. Belzaev (Reference 29) refers to the surface

and the region immediately adjacent to it as the influence zone and explains his experimental results on the basis of the influence ("active combustion") zone concept.

In the present work two hydrocarbon fuels, polyethylene and stearic acid, were compared under combustion conditions. These two materials differ primarily in their thermal stability, that is, the temperature at which they volatilize at ambient pressure. Otherwise, their physical properties are quite comparable; both are low melting, relatively high boiling, neither goes through a char on decomposing, and both are essentially saturated hydrocarbons. The burning rates obtained with stoichiometric mixtures of these fuels with AP are not greatly different. The burning rate obtained with the stearic acid is slightly faster at the lower pressures, however, the stearic acid particle size is also slightly smaller than that of the polyethylene. It appears that the ambient pressure volatilization temperature is a less important parameter than some other properties of the fuel. At elevated pressures it is likely that the energy required for volatilization and the reactivity of the species in the influence zone is more important in affecting combustion than small differences in the temperature at which volatilization occurs.

One experimental series of fuels consisted of sucrose which melts before charring, starch which chars but does not melt, and sucrose octaacetate which volatilizes leaving no residue. The burning rates from the starch and sucrose composites are almost identical (therefore, at least in this case, the effect of melting is small) while the burning rate with sucrose octaacetate is significantly lower than the other two systems. Even if fuel and oxidizer interaction are ignored, it is impossible to calculate the exact net energy released or consumed at or near the surface without a detailed knowledge of the mechanisms involved. However, a rough approximation can be made by using a very simplistic picture. If the initial sucrose decomposition can be described by a dehydration, the reaction

$$C_{12}H_{22}O_{11} \longrightarrow 12\ C + 11\ H_2O$$

would be exothermic by ∿50 Kcal/mole (Reference 31) while the vaporization of sucrose octaacetate gives a net endothermic value of several Kcal/mole. Possibly more important are the reactions subsequent to vaporization or dehydration. In the case of the sucrose octaacetate, these may occur at some distance from the surface while oxidation of the carbon residue from the sucrose occurs in close proximity to the surface. The energy from these reactions and how efficiently it is fed back to the surface would be an important factor in determining the temperature at the surface. At this time it is impossible to ascribe quantitative values to these effects, however, a summation of the approximations leads to an expected

greater net heat at the surface of the sucrose and starch composites than at the surface of the sucrose octaacetate composite.

The burning rates obtained with the carbon and paraformaldehyde composites can be explained by the same hypothesis. $(CH_2O)_X$ has the same elemental composition as the previous series. Like sucrose octaacetate, $(CH_2O)_X$ volatilizes without reacting with the AP, at least under TGA conditions. The assumption of an independent fuel and oxidizer decomposition may be modified in the combustion situation, however, with fuels containing a large percentage of oxygen this simple hypothesis may be a reasonable approximation. Carbon, which will not volatilize at any temperature attained during combustion, would be oxidized at the surface of the composite, again resulting in a larger percentage of the heat being released at the surface than when $(CH_2O)_X$ is the fuel component. The burning rates obtained with the carbon composite are close to those found with the two charring fuels, sucrose and starch. The failure of Adams (Reference 28) to obtain pressed strands with carbon was most likely due to strand pressing technique rather than anything inherent in the system.

Another fuel series used to investigate properties similar to those described above consisted of several phenolic resins. Again, the composite made with the fuel, bisphenol A, that volatilizes readily had the lowest burning rate in the series. The novalak and the resole polymers char through a dehydrogenation process, which is endothermic (~30 Kcal/mole). However, this char formation would again result in subsequent fuel oxidation reactions occurring near the surface. In addition, with these two polymers, there is the possibility for strongly exothermic reactions involving the hydrogen generated in the dehydrogenation process. It is not likely that hydrogen would diffuse very far from the surface before reacting. The fact that the resole composite burned slower than the novalak composite may be related to the unreacted hydroxymethyl groups (CH_2OH) present in the resole polymer. These could lead to further polymerization, an endothermic process, as the fuel approached surface temperatures, or a decomposition involving the hydroxymethyl groups which is more endothermic than the novalak dehydrogenation process. An alternative explanation (which must still be investigated) of the effect of the char formation on combustion is that the char is a catalyst for AP decomposition.

The working hypothesis that was used in designing the combustion experiments with various fuels is that the rate controlling reactions most likely occur at the surface of the burning composite and that the rate of these reactions is affected by the net heat release at the surface. It is noted that a composite with an aliphatic fuel such as stearic acid burns faster, especially at the higher pressures, than one with an aromatic fuel such as benzoic acid. The aromatic compound would be expected to be thermally more stable and less likely to react at the surface of the condensed phase than would the aliphatic compound. This

would result in a "cooler" surface for the aromatic composite. The burning rate pressure curves for the AP composites with aromatic fuels look very much like those of pure AP (restricted strands). Here it is interesting to note that the effect of the aromatic fuels at pressures above ~1000 psi is to lower the burning rate of the composite below that of pure AP despite the higher flame temperature attained with the composite. These data are in agreement with the hypothesis that the net heat release at the propellant surface is important in determining the rate of combustion.

The variation in thermal and oxidative stability for a series of aromatic compounds (hydroquinone, benzoic acid and isophthalonitrile) was not sufficient to appreciably affect the composite burning rate. The one notable difference was the increase in the burning rate pressure exponent above 2000 psi with isophthalonitrile as a fuel. This increase in pressure exponent above 2000 psi will be noted later with several other fuels.

Triphenylmethane was the only fuel which significantly affected the pressure exponent below ~1000 psi except for those fuels whose decomposition products (e.g., H_2O, NH_3) would be expected to directly affect the AP combustion mechanism. Here it is possible that a relatively stable free radical is generated which can react with the AP in such a way as to interfere with the AP dissociative evaporation mechanism. Whether this affect disappears at higher pressures due to a change in the thermal decomposition of triphenylmethane or due to the AP combustion mechanism changing with pressure is not known; however, at the present time we prefer the latter explanation.

The remaining fuels differ from those already discussed in that they can decompose at temperatures below the surface temperature of an AP composite into products which could affect the combustion mechanism of AP. In the present study these compounds were certain amides, diamides and acid amides. Of the amides both benzamide and acetamide can decompose to yield NH_3 and a ketone or H_2O and a nitrile. Previous work (Reference 6) with NH_3 releasing compounds showed that their effect was greatest at pressures below 1000 psi, however, it was never clear whether this was due to a change in the AP combustion mechanism or the fact that at the higher pressure the inorganic salt would not dissociate into free NH_3.

The AP benzamide composite burns with a very low pressure exponent over a large pressure range (200-2000 psi). This involves both a burning rate depression at the higher pressures and an increase in rate at the lower pressures. It has been observed in the earlier work with NH_3 releasing salts that the NH_3 had very little effect at atmospheric pressure, in fact it seemed to aid ignition and result in a small increase in burning rates at the low pressures.

The acetamide composite would not sustain combustion between ~100 and 600 psi. As with the benzamide composite the burning rate pressure exponent is low from 1000 to 2000 psi after which there is a relatively

rapid increase in burning rate with pressure. It is interesting to note that one possible product of decomposition for both the benzamide and the acetamide is a nitrile and that the isophthalonitrile composite exhibited the same sharp increase in burning at pressures above 2000 psi.

Unlike the amides there is essentially only one thermal decomposition path for the diamides. The products of this reaction are the corresponding imide and ammonia. The succinamide has resulted in the slowest burning AP composite so far tested. The reduction in burning rate was dramatic with a change of almost an order of magnitude over many composites (e.g. ∿0.015 inches/sec at 15 psi to ∿0.07 inches/sec at 3000 psi). The phthalamide composite has a higher burning rate than the equivalent succinamide composite; however, the burning rate is significantly lower than that of composites with aromatic fuels such as benzoic acid. Phthalamide is unique in the series of fuels yielding NH_3 or H_2O on decomposition in that the maximum burning rate occurs at ∿800 psi above which pressure the burning rate has a negative pressure exponent. The results from these last two composites indicate that NH_3 released at the right point in the temperature profile has a signficiant effect on the burning rate. The addition of a CuO202 catalyst to the succinamide composite drastically altered its combustion characteristics. The burning rate increased at all pressures and the pressure exponent was positive and essentially constant over the entire pressure range tested. These results are consistent with earlier laboratory and combustion data which indicated an ammonia atmosphere had no effect on AP decomposition if a copper catalyst was present (Reference 1).

The thermal decomposition of phthalamic acid is similar to that of the diamides in that an imide is formed; however, the condensation produces H_2O rather than NH_3. The burning rate of the phthalamic acid composite is pressure independent from 300 to 1500 psi. At pressures above 1500 psi the burning rate of this composite increases rapidly with pressure. This burning rate pressure profile is similar to that found when benzamide is the fuel and may indicate that the non-organic product in both cases is H_2O.

It is interesting to note that all the AP composites containing fuels which have a nitrile functional group or decompose to form a product containing a nitrile (acetamide, benzamide, phthalamic acid, and isophthalonitrile) have a positive break in the burning rate pressure exponent at ∿2000 psi. The one exception appears to be phthalamide which did not burn above ∿1500 psi. The problem may have been one of ignition as there were several pressure surges with this composite at 3000 psi when the igniter size was increased. A similar positive break in the pressure exponent has been noted at these pressures with composites containing permanganated AP. The latter system clearly involves condensed phase reactions. Similarly, laboratory work has shown that a condensed phase reaction can occur between perchlorate ion and CN^- groups although it has not yet been shown whether such a reaction would occur under combustion conditions.

Reduction of Perchlorate Ion and Perchloric Acid - If a significant step in the catalytic decomposition of AP, under combustion conditions, is the reduction of perchlorate ion or perchloric acid by the catalyst, then the thermodynamic potential for this step may be an important factor. Using this criteria, a great many transition metal compounds in their more stable oxidation states can be eliminated as combustion catalysts. The potential to reduce perchlorate ion is not a completely sufficient criterion for an AP combustion catalyst, however, if the catalyst does not have this potential its likelihood of being a good combustion catalyst is greatly diminished. This selection rule is not contradicted by any presently available data. Using Figure 33, as an illustration, an exothermic condensed phase reaction took place between Cu_2O and $KClO_4$ but not between CuO and $KClO_4$. In this situation the cuprous oxide is a reactant and not a catalyst as there is no way to regenerate cuprose oxide after it has been oxidized to cupric. If the oxidant had been AP, the NH_3 could reduce the cupric back to the cuprous state. For catalytic purposes there must be a reaction in which the catalyst can be reduced back to its lower oxidation state. If the $KClO_4$ - Cu_2O mixture is heated in the presence of an organic fuel, the decomposition of the $KClO_4$ goes to completion.

It is interesting to note that if the thermodynamic potential is favorable for such a reaction, non-metallic salts will also reduce perchlorate ion in a condensed phase reaction. When $KClO_4$ is reacted with KCN, KSCN, and KOCN, the reaction goes essentially to completion. Since these additives can also act as a 'fuel' with many reactive intermediate possible, this is not particularly surprising. When there is good physical contact such as with KSCN, which melts below the reaction temperature, the decomposition reaction can go into a detonation. It is also interesting that all of these reactions occur after the $KClO_4$ phase transition at which the perchlorate ion starts to rotate. All of these reactions are strongly exothermic by ~400°C which is the temperature at which the AP high temperature reaction begins. Whether this redox reaction is important during combustion depends both on the kinetics and the reaction pathways available. Even if the thermodynamic potential for such a reaction is favorable, the reaction will not occur if it is not kinetically fast enough for the time periods involved in combustion. To determine this requires further experimental work.

The importance of the reaction path is well illustrated by the AP - $KMnO_4$ system. AP - $KMnO_4$ is thermally less stable than AP, that is, it decomposes faster and at lower temperatures than AP, but during combustion it burns slower than pure AP. This is most likely due to the nature of the reaction products and their effect on flame temperature, etc. The area holds promise for interesting ways to vary the combustion rate of an AP composite propellant.

CONCLUSIONS

An important generalization that can be made based on the experimental results obtained in the current program is that the log pressure log burning rate plot for most AP composites is not a straight line over a very large pressure range. The Summerfield equation (Reference 27) turns out to apply to a very limited number of fuels over a relatively short pressure range (∿200-1000 psi). In the past this has been adequate as the fuels used and the pressure range of interest was such that a fair number of data fit this empirical correlation. However, at no point was the equation useful as a predictive tool. From the experimental results, with the AP-fuel composites studies in this program, it is apparent that it will be difficult if not impossible to derive a burning rate equation which will fit a great variety of different fuels or even one that will fit a given fuel over a large pressure range. We have, therefore, attempted to develop a qualitative explanation or description of the combustion of AP composites in such a manner that it will be possible to make predictions on what a given composite will do at a given pressure or maybe more important what properties the fuel or fuel catalyst system must have to meet the combustion requirements of a given mission.

At this time it would be premature to assimilate these data into a unified theory of AP composite combustion, however, a great deal of the data does fit the general working hypothesis for combustion suggested at the end of the previous program. Those fuels which interfere with the AP dissociative evaporation process have their greatest effect on the burning rate at the lower pressures while those which may involve condensed phase reactions have their greatest effect on the reaction rate at the higher pressures. These ideas added to the concept of a net heat balance (zone of influence) at the surface of a burning propellant hold promise of developing into a useful (predictive) description of the combustion process in an AP composite propellant.

It is difficult to design combustion experiments for a specific effect of the fuel component as very little data exists on the pyrolysis of most organic compounds. What data are available generally have been determined at atmospheric and sub-atmospheric pressures. Therefore, there is always doubt (especially when the variable of heating rate is also considered) as to how the organic material behaves under combustion conditions. This does not mean that one cannot correlate the combustion data with the properties of the fuel but it does mean that one has to be careful in extrapolating data obtained for example with a DTA to the combustion conditions.

The following is a summary of the more important experimental results observed in the current program.

1. The combustion rate of pure AP, determined with 38mm diameter pressed powder discs, has a constant positive pressure exponent between 1200 and 3000 psi, i.e., there is no evidence for a negative pressure exponent in this pressure region if the AP surface area to perimeter ratio is large enough.

2. The AP low temperature decomposition, 200-300°C, is negatively catalyzed by phosphate and positively catalyzed by chlorate. The phosphate may affect the rate of surface diffusion of $HClO_4$ and thereby the bimolecular reaction of $HClO_4$ to gaseous products. The decomposition of AP containing 0.025% chlorate is approximately an order of magnitude faster than pure AP and the decomposition proceeds by a different, or at least modified, reaction mechanism from that found with pure AP.

3. The phosphate and chlorate or their decomposition products do not appear to affect the dissociative evaporative rate of the AP residue which is left after the low temperature decomposition.

4. Additives, such as phosphate and chlorate, which catalyze the AP low temperature decomposition by as much as an order of magnitude have only a limited effect (from 2 to 18%) on the combustion rate of pressed AP strands. Pressed AP strands containing a relatively high concentration of phosphate (0.64%) have a smaller change in their burning rate pressure exponent near 1000 psi than strands of pure AP.

5. Those reactions which affect the combustion rate of a composite propellant occur near or on the surface of the composite, i.e., in the zone of influence. That is, the surface temperature and therefore the combustion rate is a function of the sum of the heat flux to the surface, heat losses from the surface and the net heat from all the reactions (exothermic and endothermic) at the surface.

6. A composite with a relatively unreactive fuel such as benzoic acid has a lower burning rate than a similar composite with a more reactive aliphatic acid such as stearic acid. At pressures above ~1000 psi the burning rate of the benzoic acid composite is lower than that of pure AP.

7. Composites with fuels which char on decomposition have higher burning rates than composites with similar fuels which volatilize without charring. This has been demonstrated both for a series of fuels in which char occurs by dehydration and in a series of fuels which char by dehydrogenation. A dual and possibly overlapping explanation is possible: (1) the decomposition mechanism providing the char, and subsequent oxidative consumption, is more exothermic in the 'zone of influence' than volatilization and (2) the char is a catalyst for AP

decomposition.

8. Fuels which thermally decompose, at temperatures below the composite surface temperature, to form NH_3 or H_2O significantly affect the combustion rate of AP composites at all pressures. Included in this list of fuels are amides, diamides and acid amides. Generally these fuels lower both the burning rate and the burning rate pressure exponent.

9. There are ions which have both the thermodynamic potential and the kinetic reactivity to reduce perchlorate ions in a solid-solid or solid-liquid reaction. Such ions as CNO^-, CN^- and SCN^- all react with $KClO_4$, in a DTA, to cause deflagration and detonation above the temperature (300°C) at which the ClO_4^- ion begins to freely rotate.

10. Composites containing fuels with functional groups which have the potential to reduce the perchlorate ion (e.g. nitriles) generally have relatively large burning rate pressure exponents above ∿2000 psi.

11. Small amounts of $KMnO_4$, whether isomorphously substituted in the AP or mechanically mixed with the AP, drastically affect the combustion of AP. If the pressed strands are not restricted, combustion cannot be sustained at any pressure tested (15-3000 psi). With a restricted strand,combustion is sustained at all pressures tested, however, the combustion rates are lower than those for pure AP.

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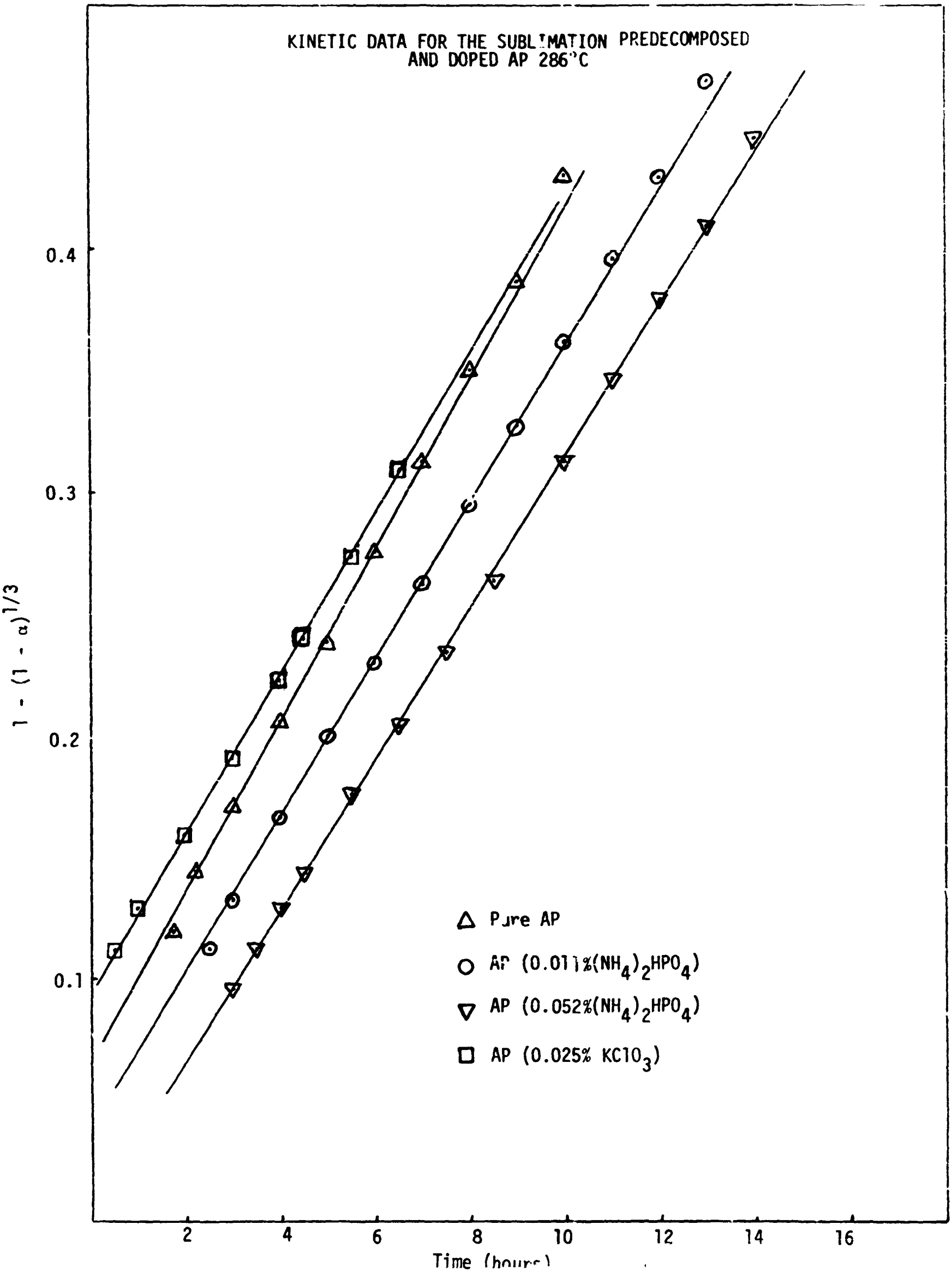
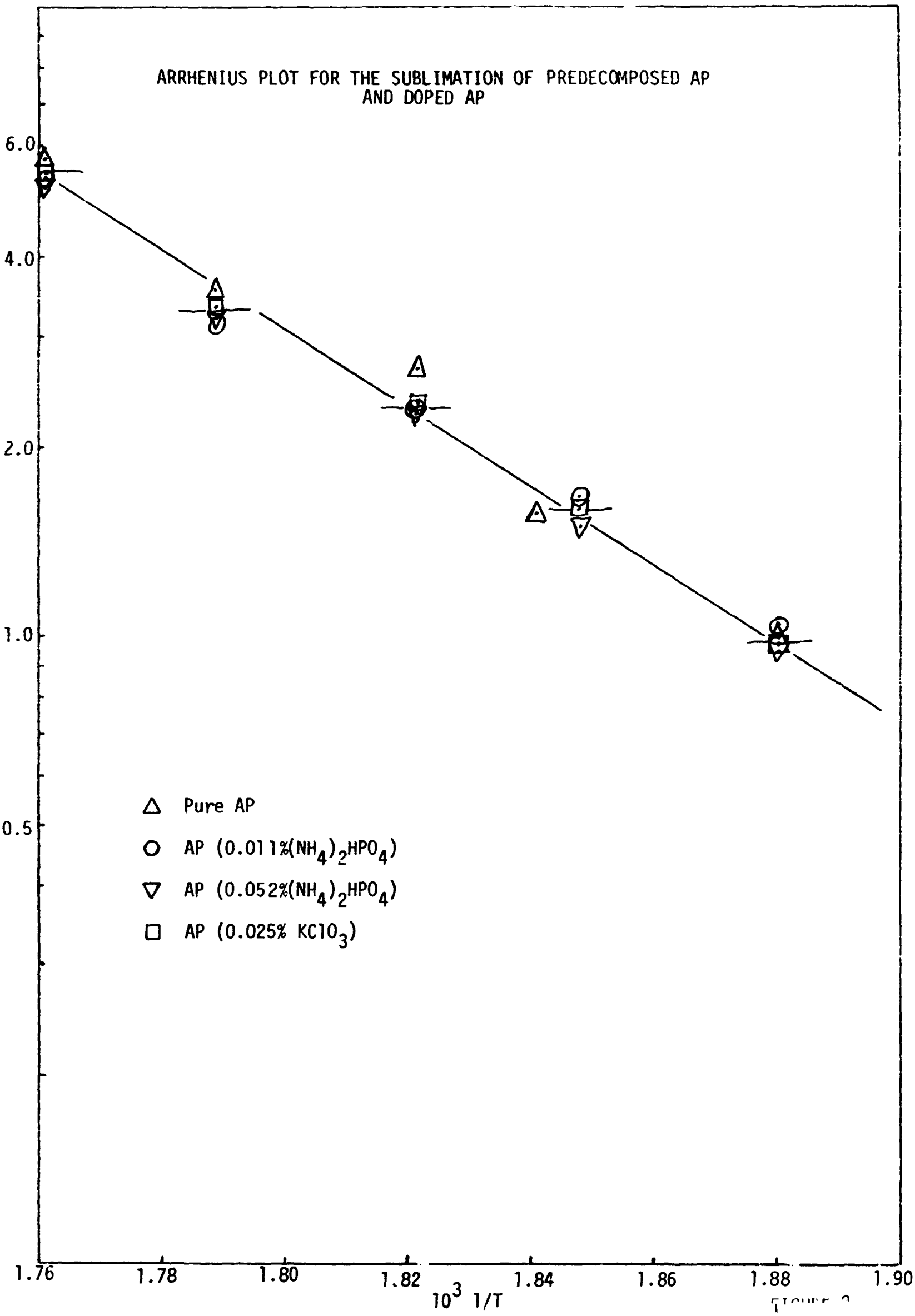

KINETIC DATA FOR THE SUBLIMATION PREDECOMPOSED AND DOPED AP 286°C
1 - (1 - α)^1/3
0.4
0.3
0.2
0.1
2
4
6
8
10
12
14
16
Time (hours)
Pure AP
AP (0.011%(NH4)2HPO4)
AP (0.052%(NH4)2HPO4)
AP (0.025% KClO3)


ARRHENIUS PLOT FOR THE SUBLIMATION OF PREDECOMPOSED AP AND DOPED AP
6.0
4.0
2.0
1.0
0.5
10^4 k min.$^{-1}$
Pure AP
AP (0.011%$(NH_4)_2HPO_4$)
AP (0.052%$(NH_4)_2HPO_4$)
AP (0.025% $KClO_3$)
1.76
1.78
1.80
1.82
1.84
1.86
1.88
1.90
10^3 1/T

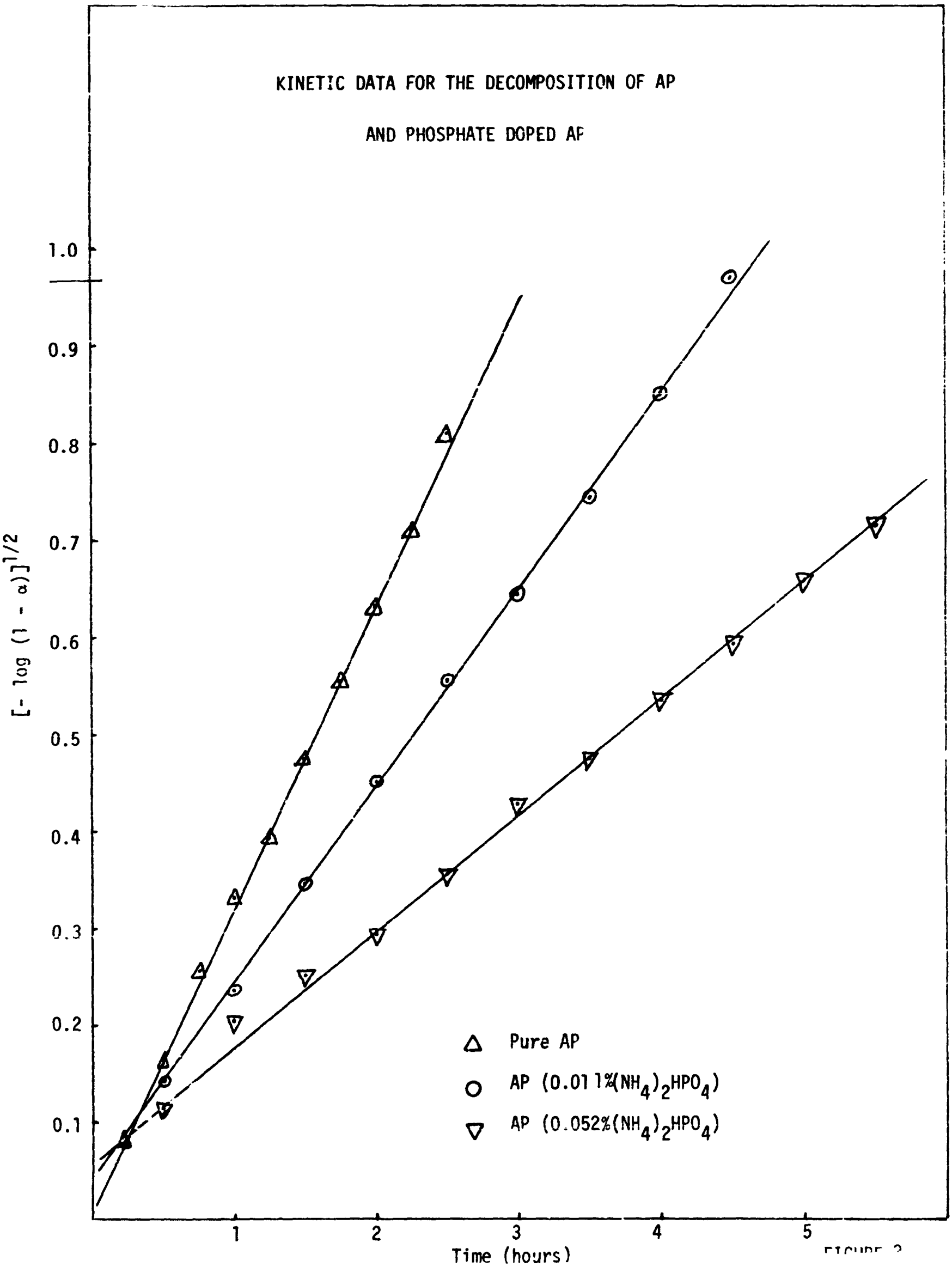
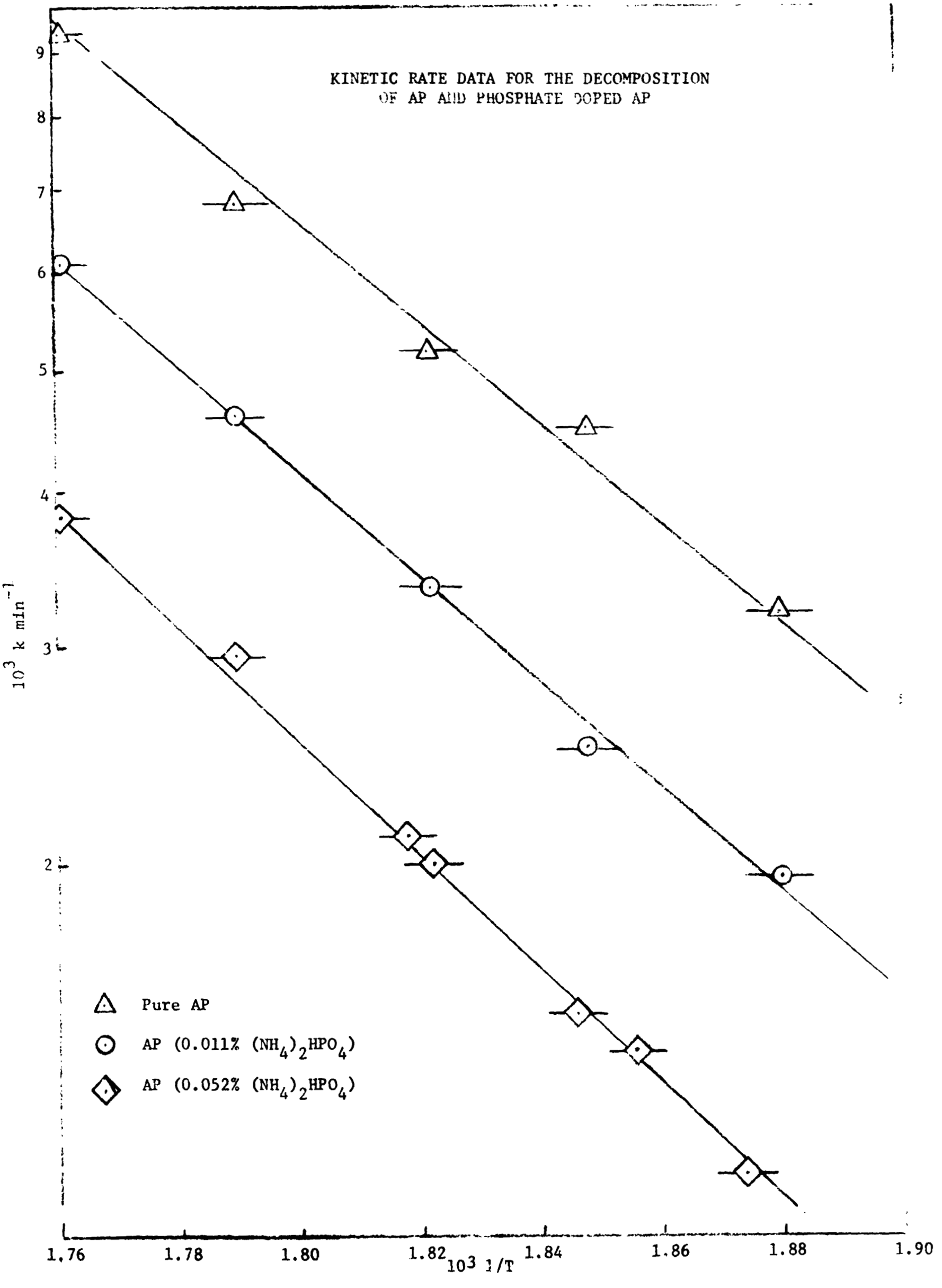
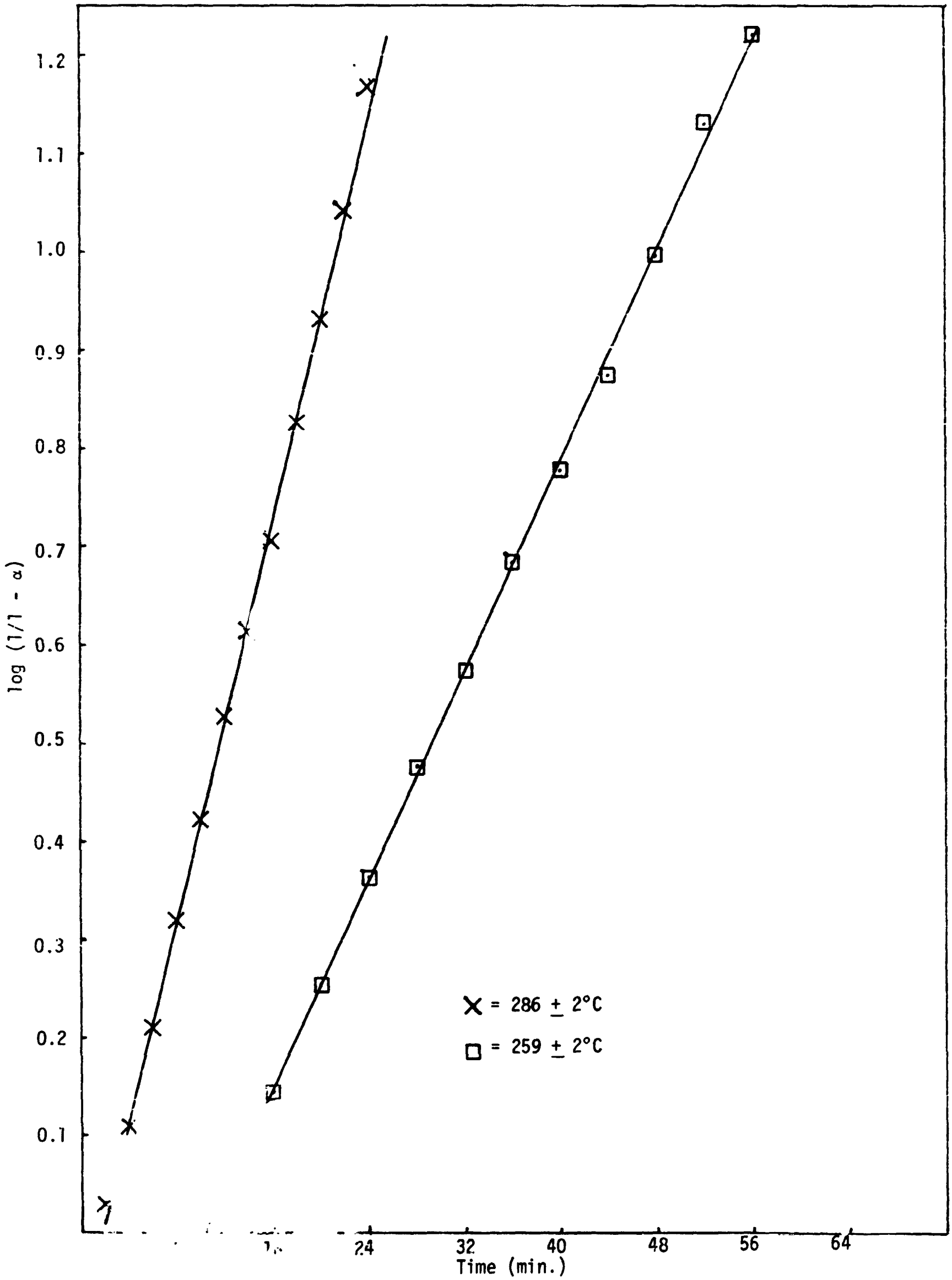

KINETIC DATA FOR THE DECOMPOSITION OF AP
AND PHOSPHATE DOPED AP
[- log (1 - α)]^1/2
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
Time (hours)
Pure AP
AP (0.011%(NH4)2HPO4)
AP (0.052%(NH4)2HPO4)

FIGURE 3

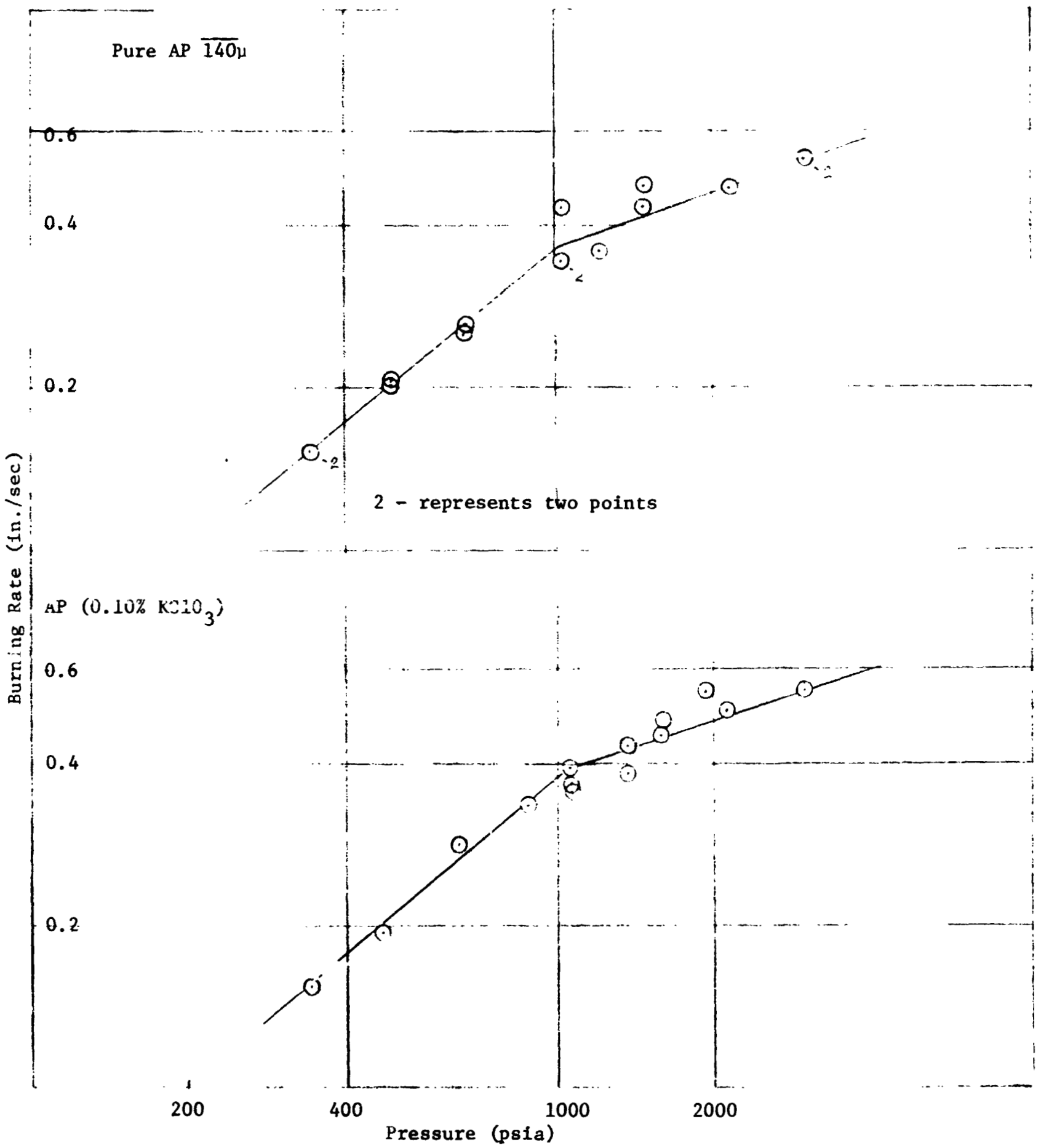
KINETIC RATE DATA FOR THE DECOMPOSITION
OF AP AND PHOSPHATE DOPED AP



KINETIC RATE DATA FOR THE DECOMPOSITION OF CHLORATE DOPED (0.025%) AP



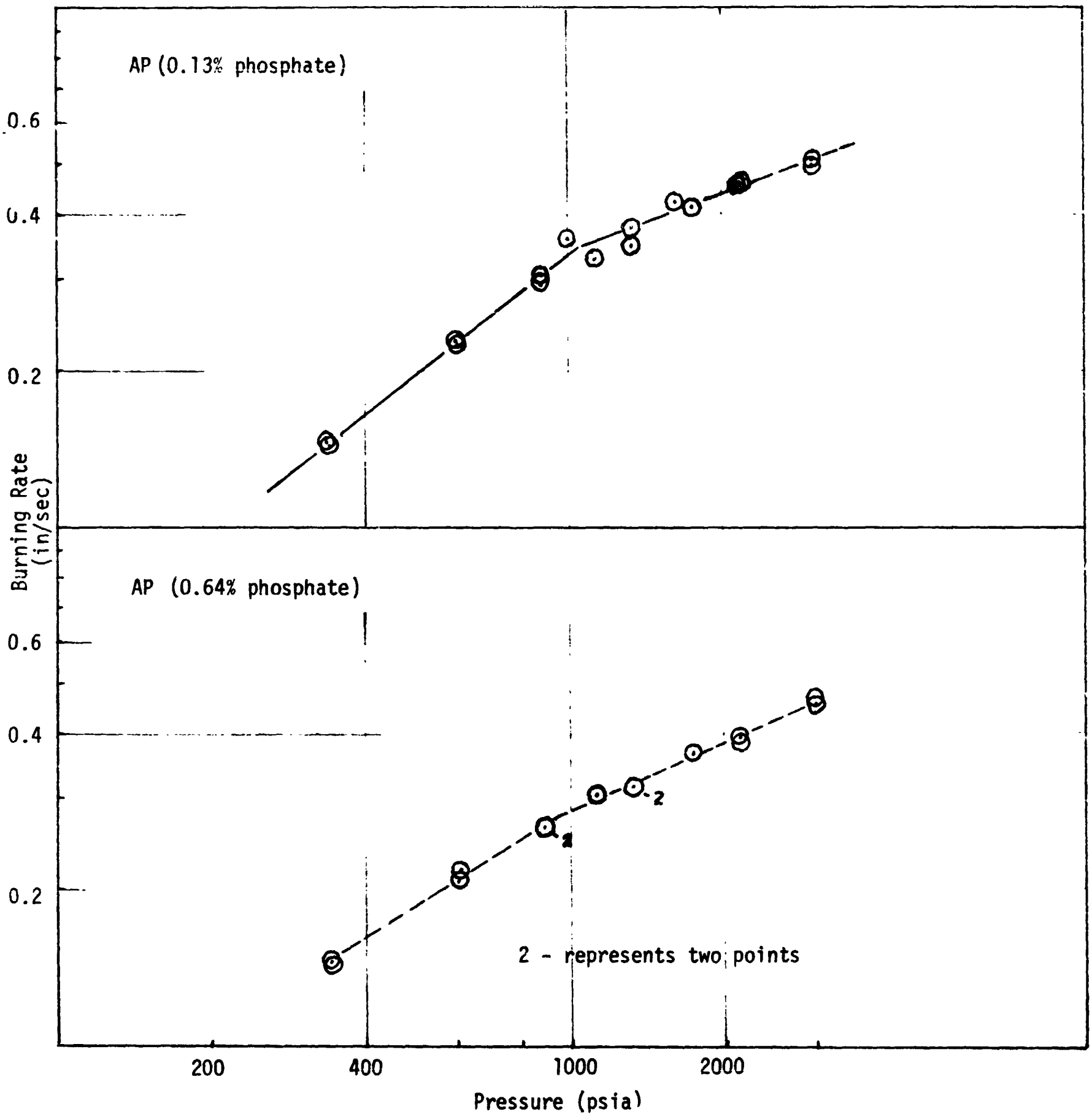
BURNING RATE DATA FOR AP AND CHLORATE DOPED AP[a]



(a) All data were obtained with pressed strands whose sides were restricted with a polymeric material.

Figure 6

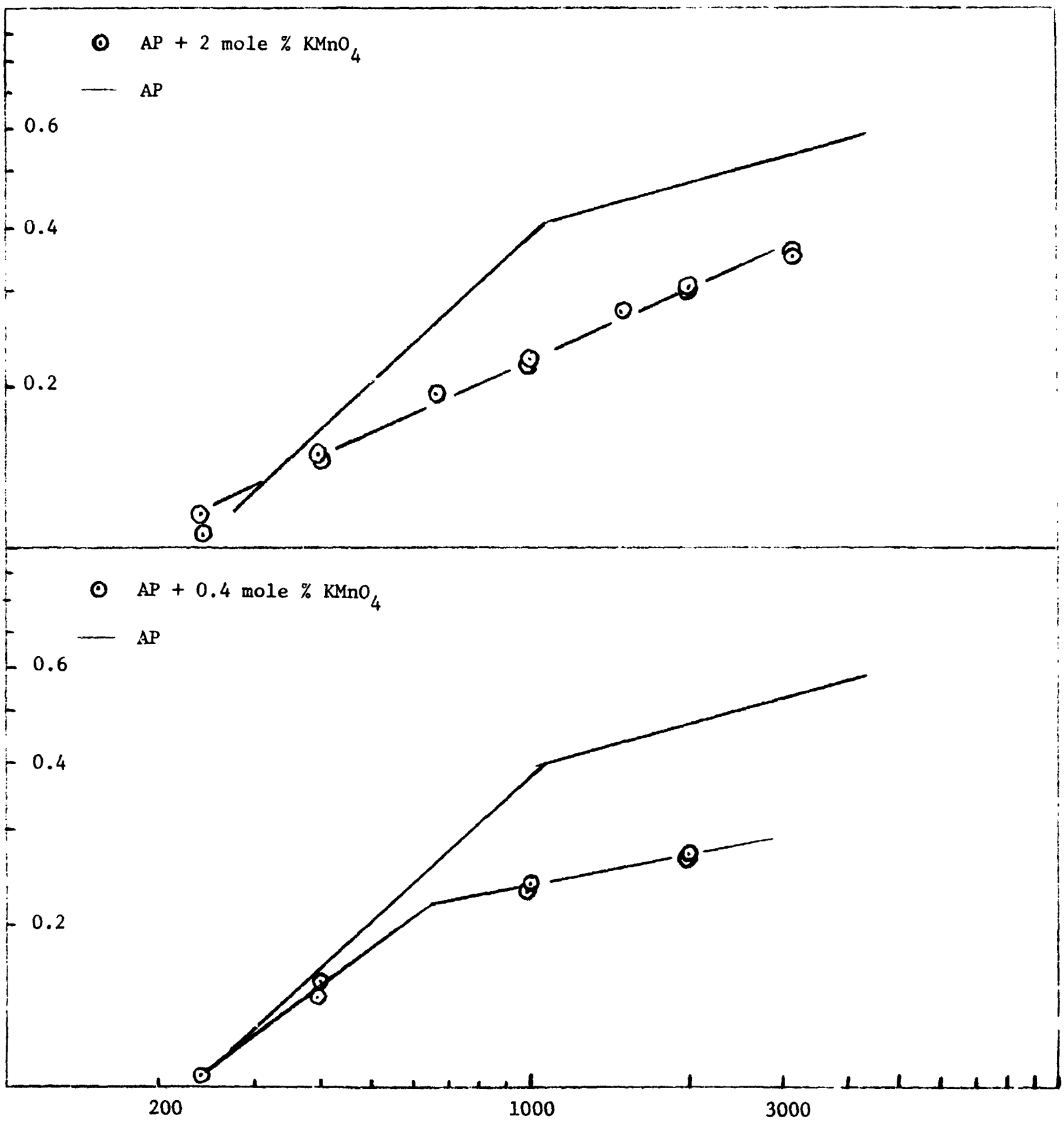
BURNING RATE DATA FOR PHOSPHATE DOPED AP [a]



(a) Same as Figure 6

FIGURE 7

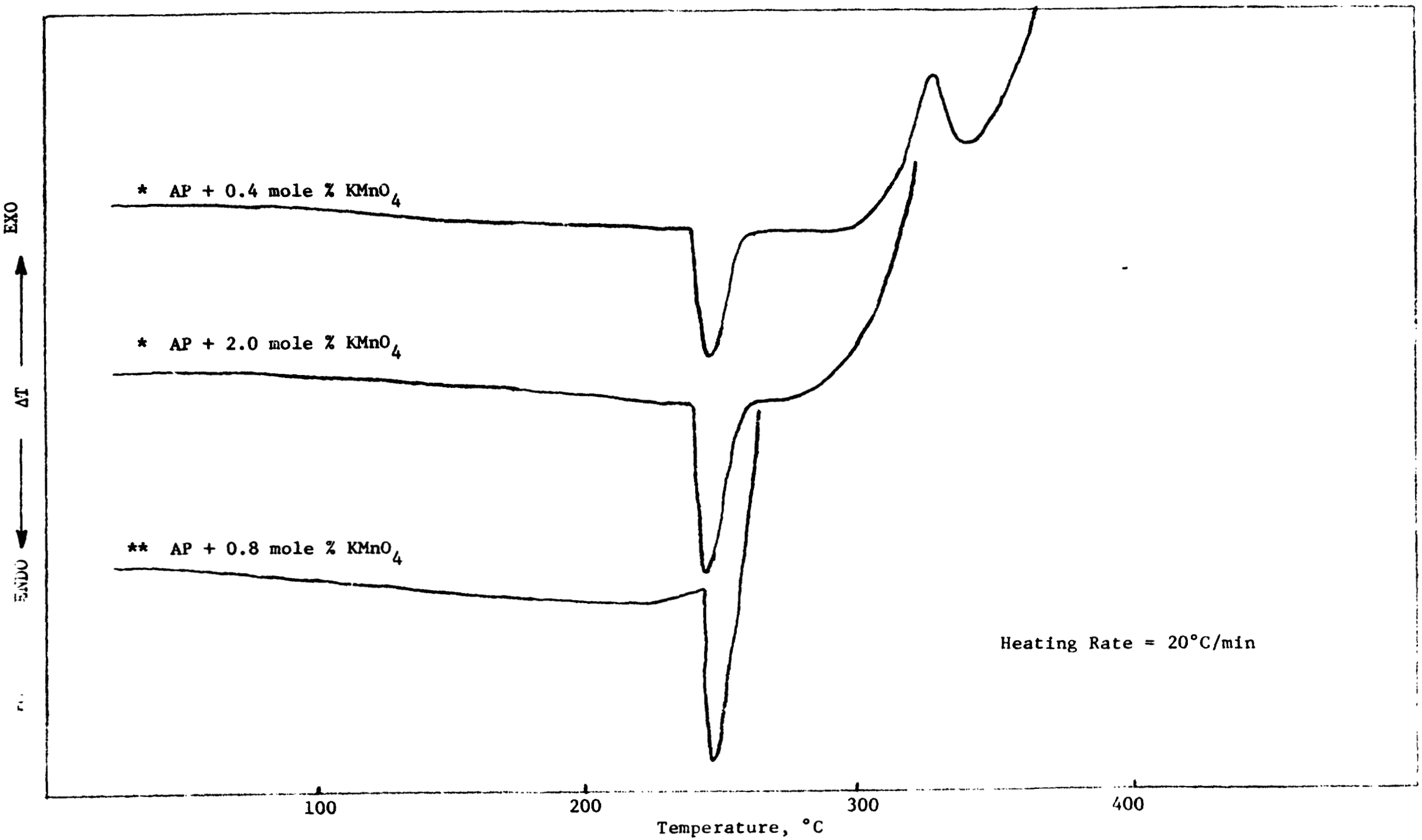
BURNING RATE OF PRESSED MECHANICAL MIXTURES OF AP AND $KMnO_4$ (a)



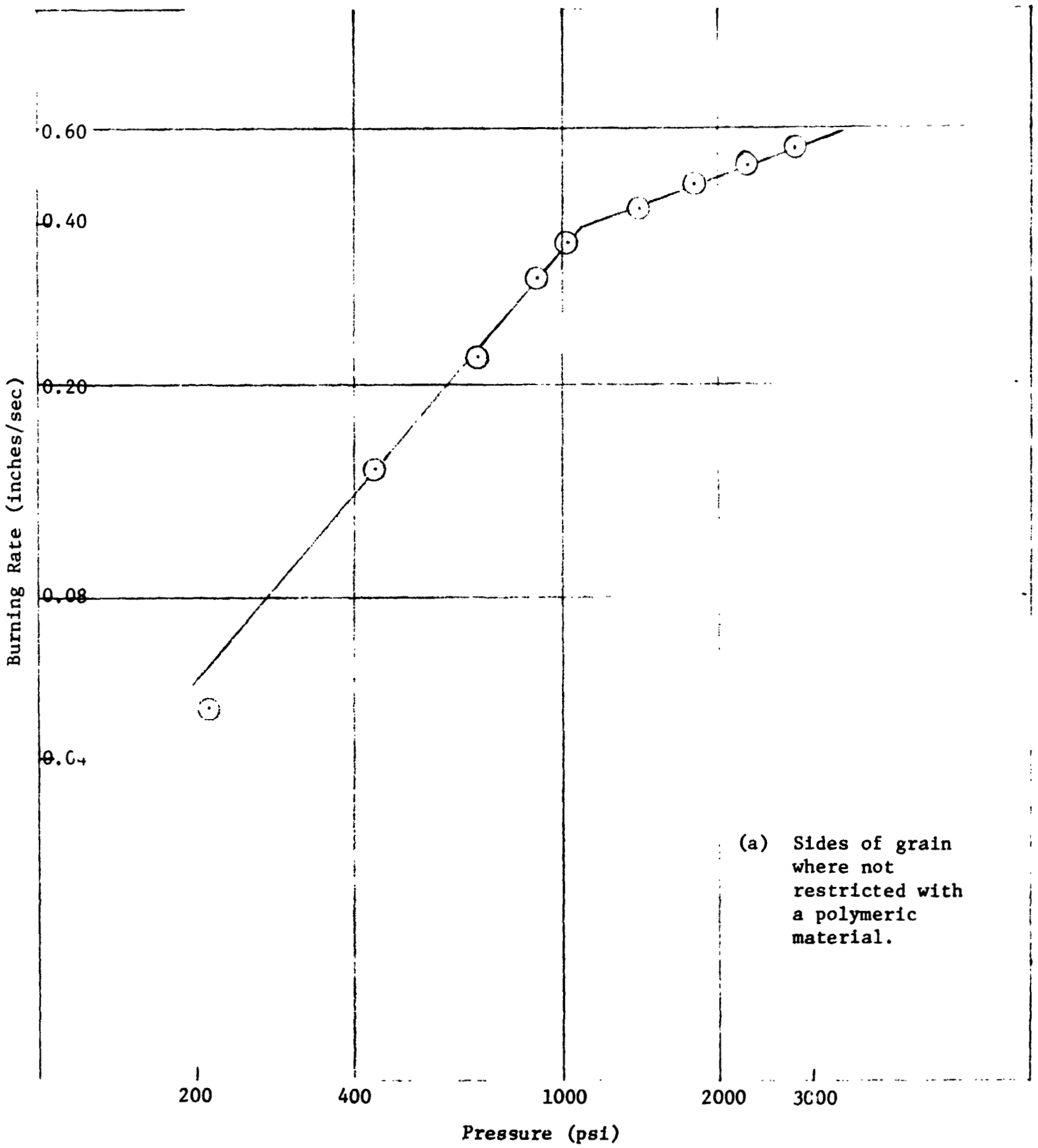
(a) Same as Figure 6

Figure 8

DTA's OF AP MECHANICALLY MIXED* AND ISOMORPHOUSLY SUBSTITUTED** WITH $KMnO_4$



BURNING RATES OBTAINED FROM PRESSED, 38MM DIAMETER, AP GRAINS[a]



(a) Sides of grain where not restricted with a polymeric material.

Figure 10

THERMOGRAVIMETRIC TRACE OF POLYETHYLENE AND STEARIC ACID

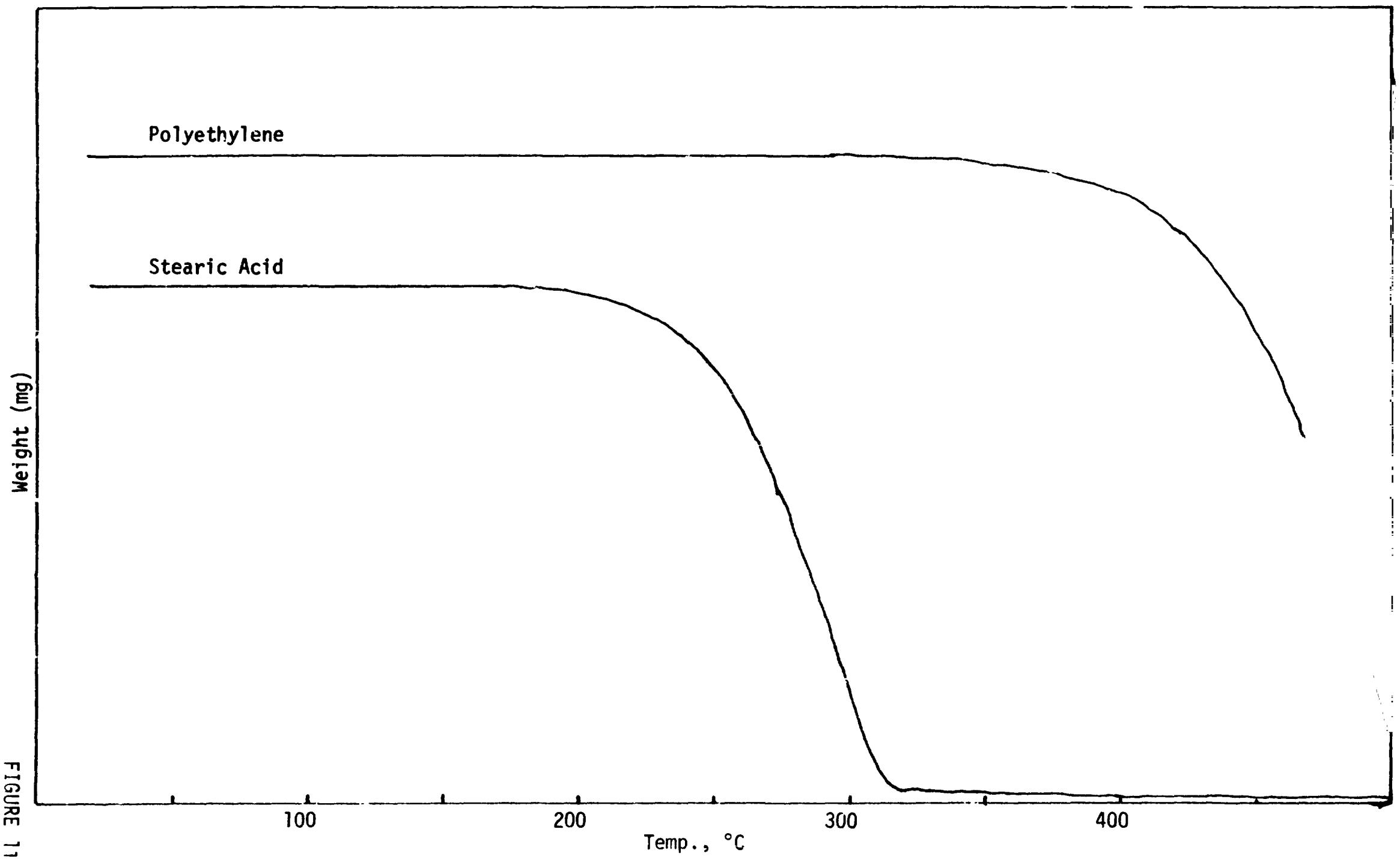


FIGURE 11

AP-POLYETHYLENE AND AP-STEARIC ACID PRESSED STRAND
BURNING RATES

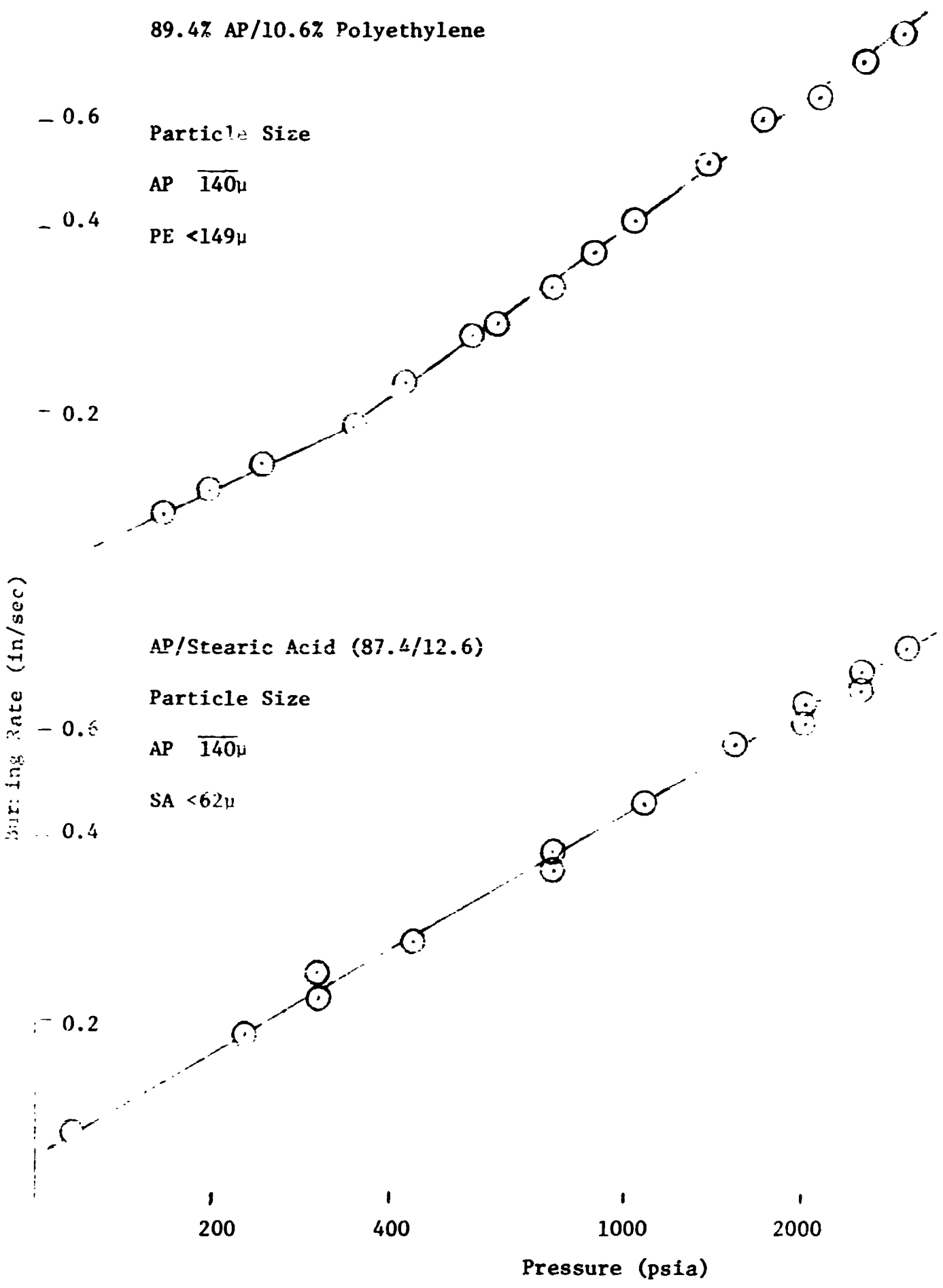
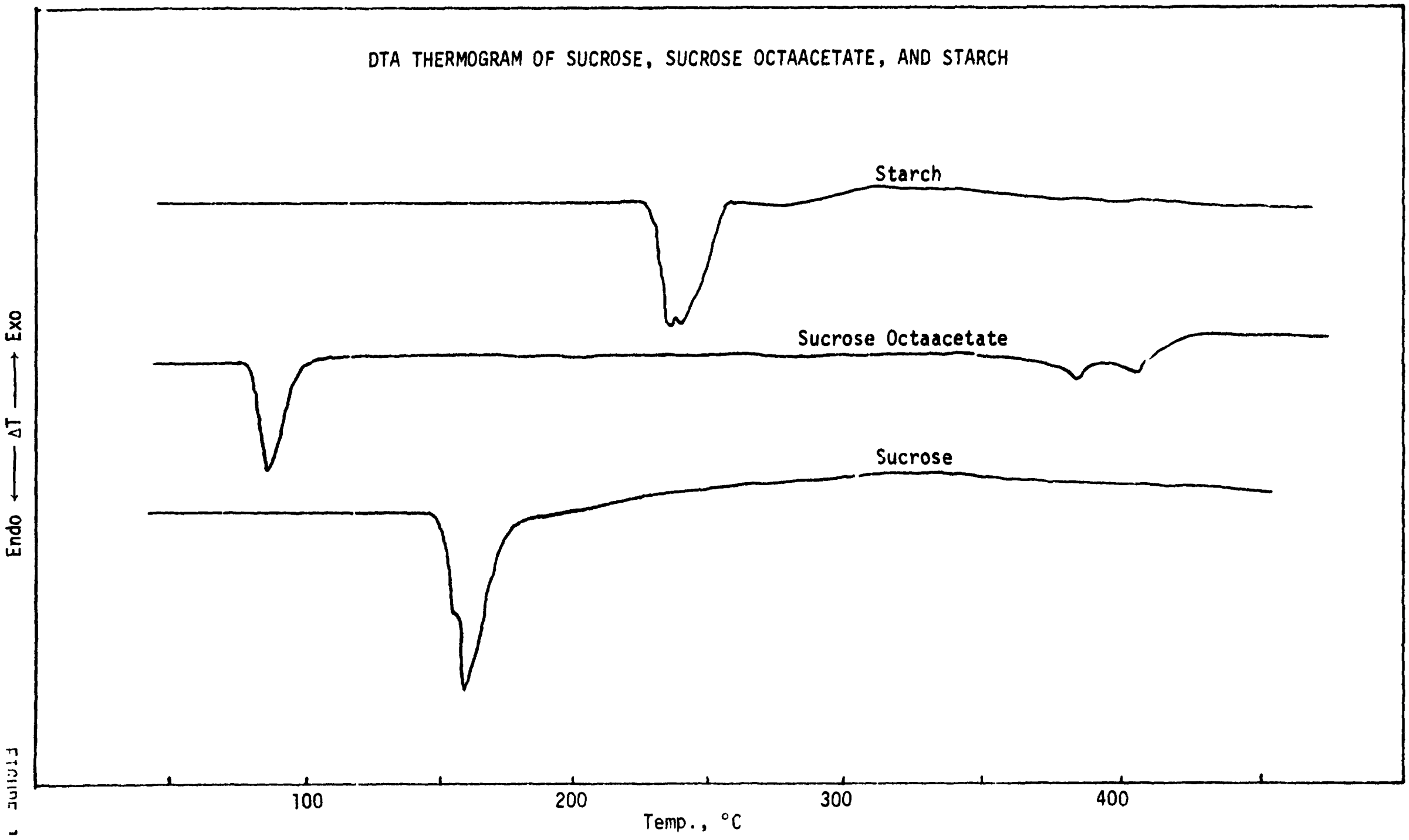
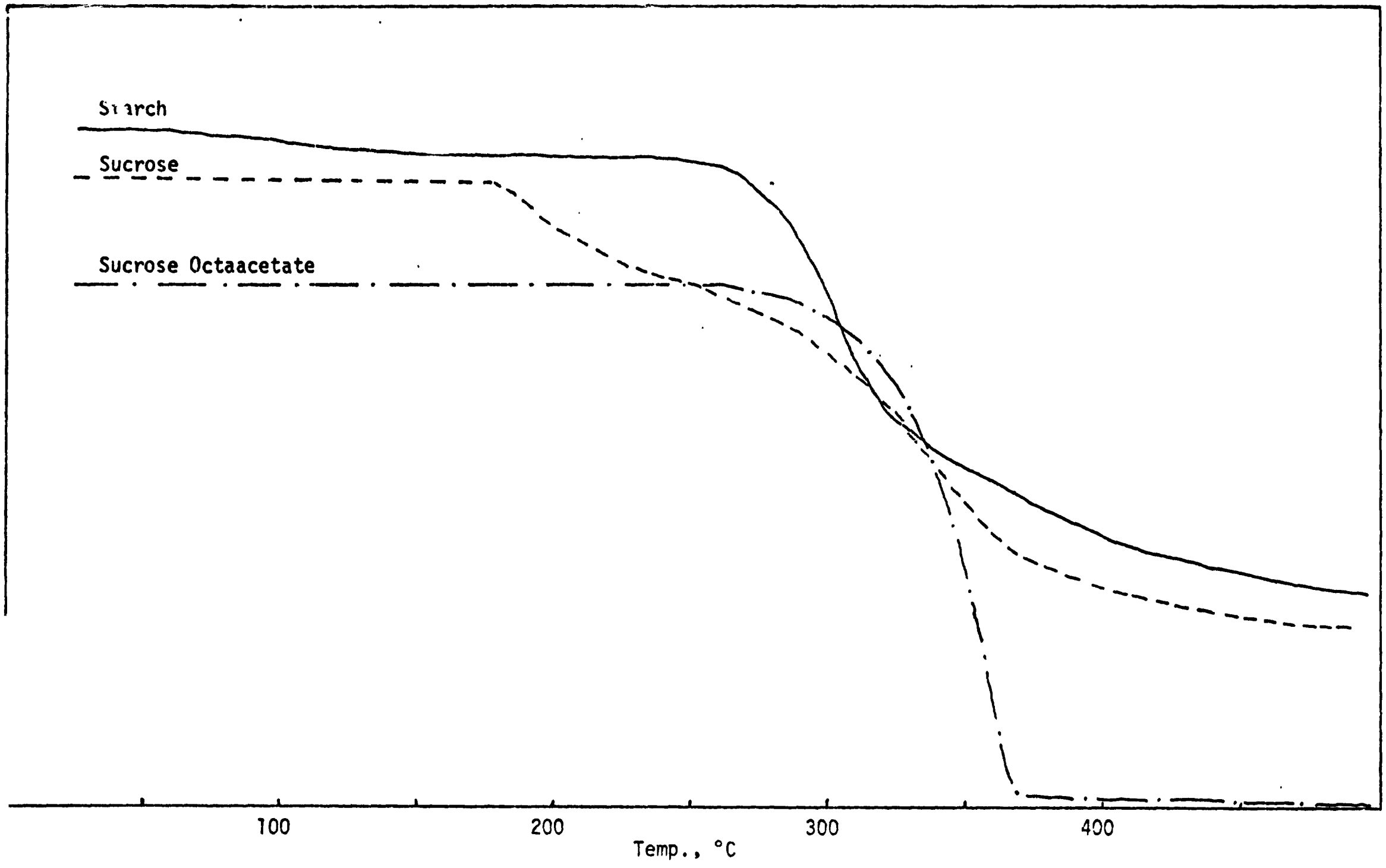


Figure 12

DTA THERMOGRAM OF SUCROSE, SUCROSE OCTAACETATE, AND STARCH



THERMOGRAVIMETRIC DECOMPOSITION OF SUCROSE, SUCROSE OCTAACETATE, AND STARCH



TGS'S OF AP, SUCROSE, AND AP SUCROSE OCTAACETATE MIXTURES (75/25)

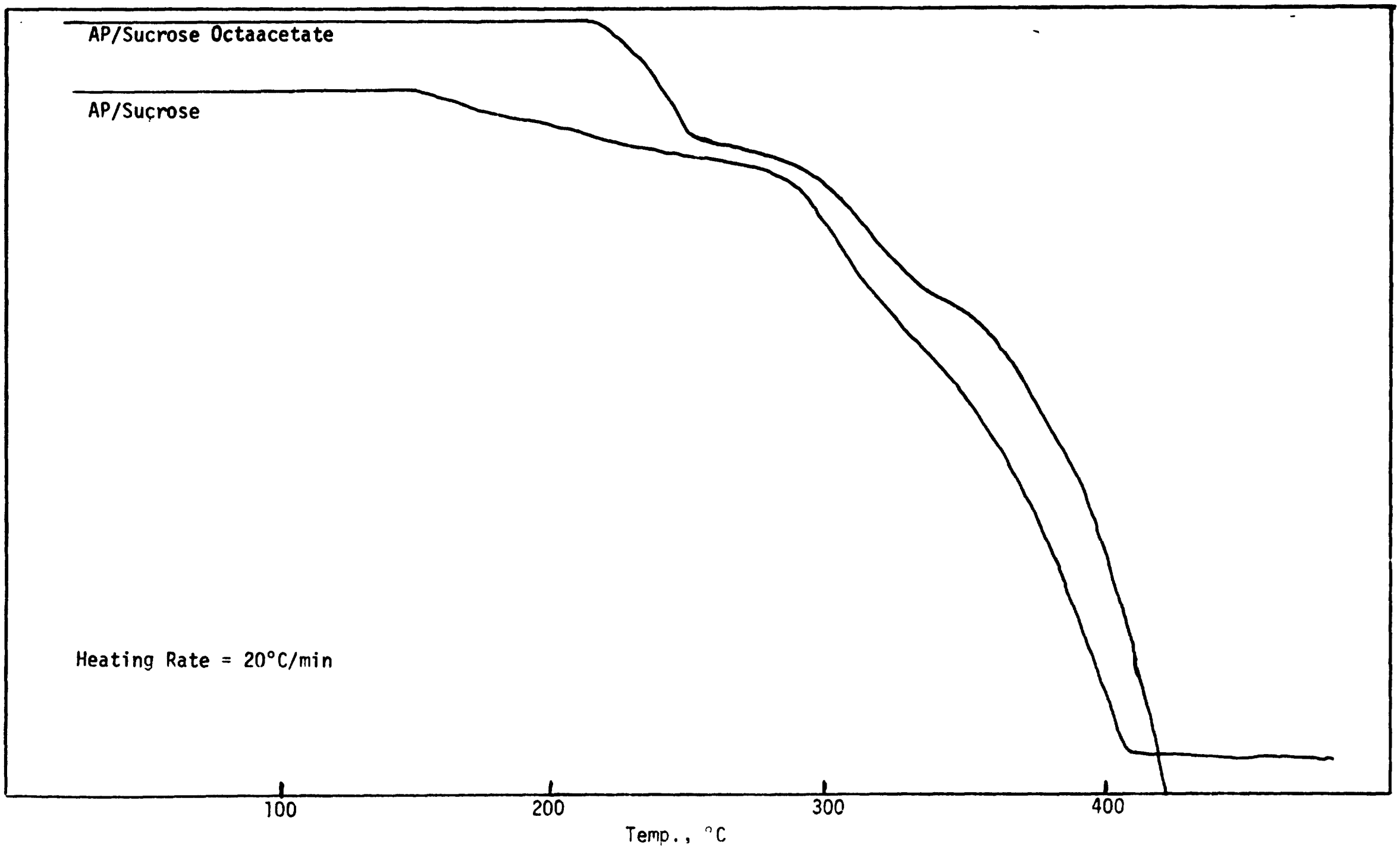


Figure 1

BURNING RATES OF PRESSED POWDER STRANDS
OF AP WITH SUCROSE, STARCH, AND SUCROSE OCTAACETATE

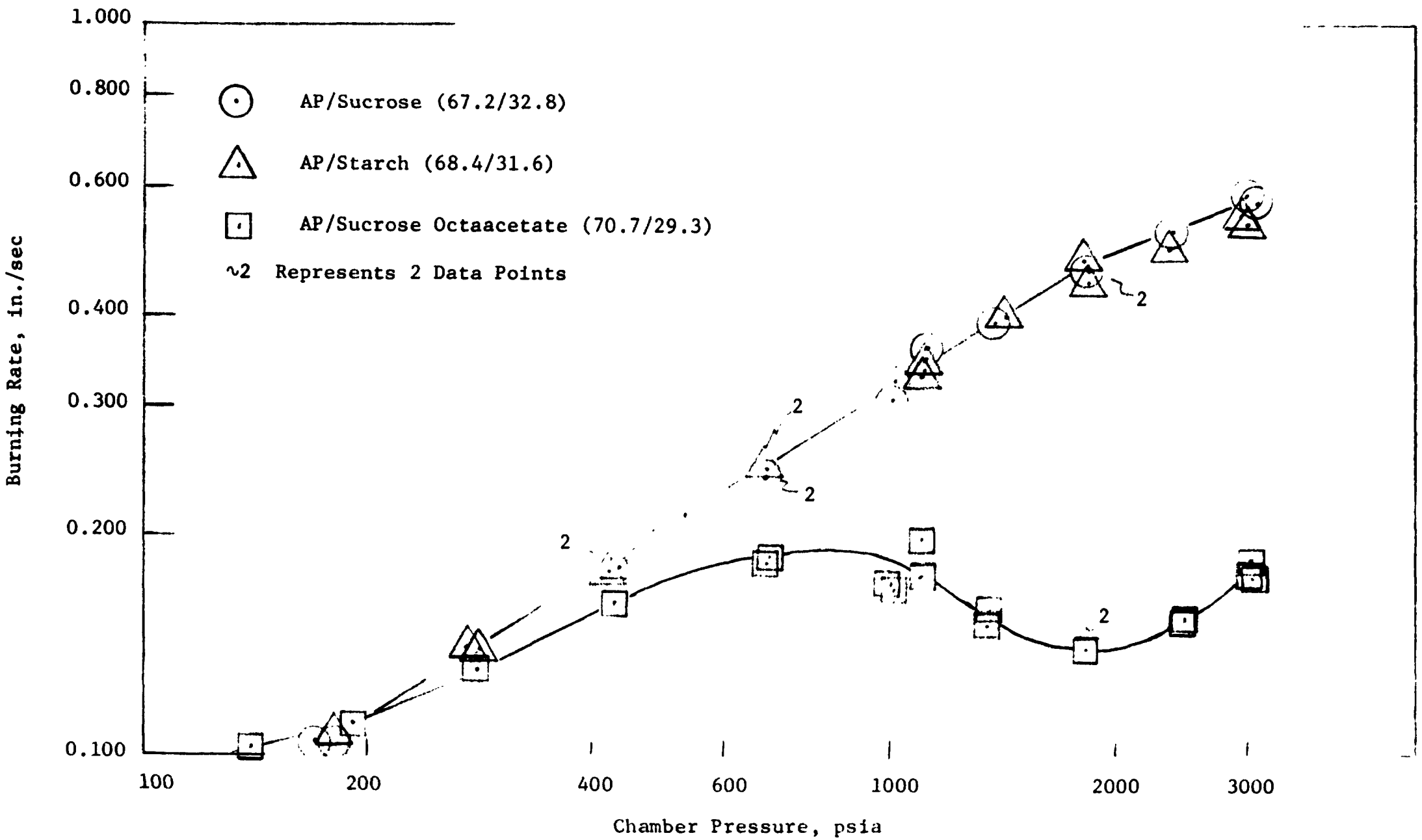
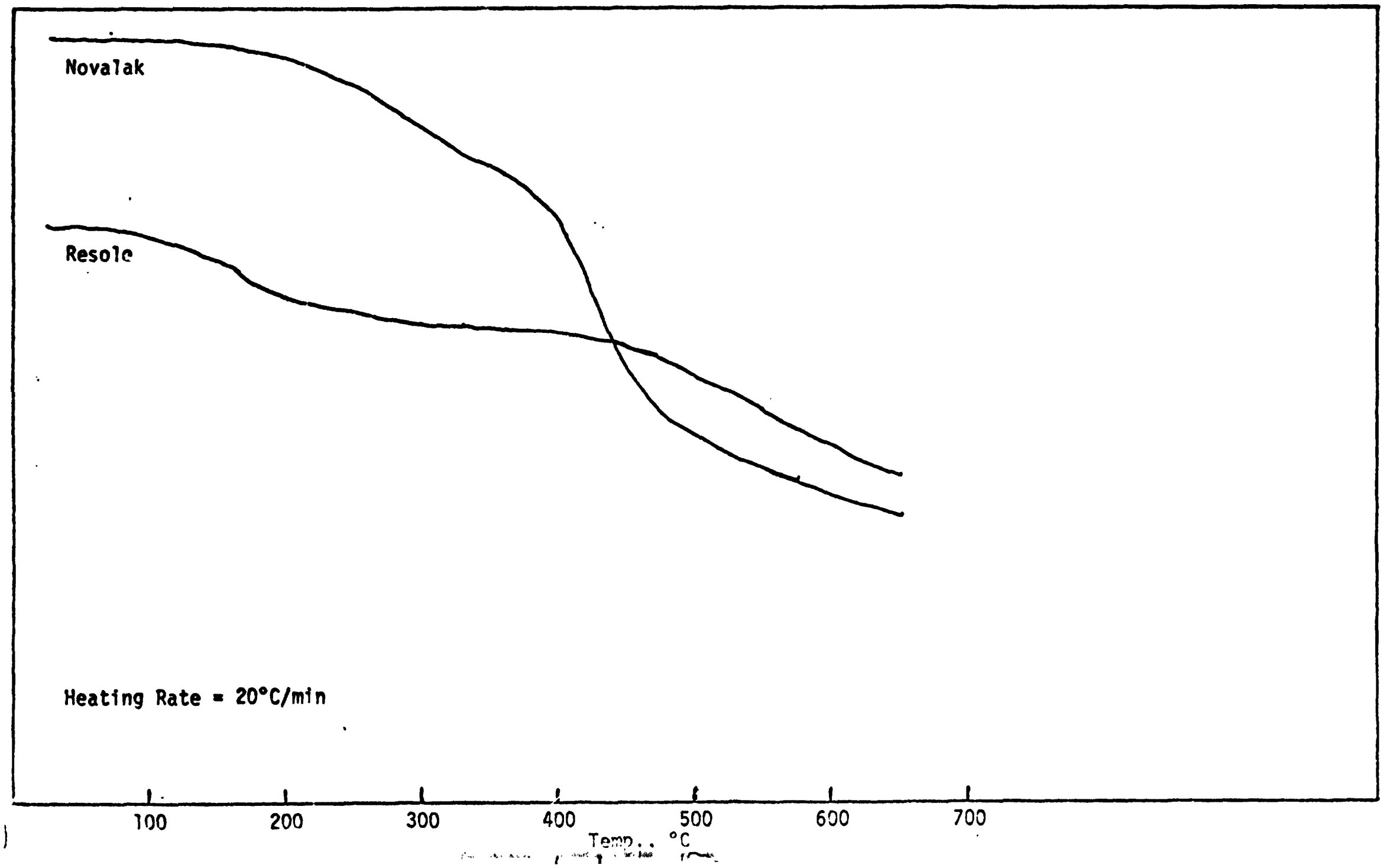


Figure 16

TGA'S OF NOVALAK AND RESOLE



TGA'S OF AP WITH CARBON AND WITH NOVALAK

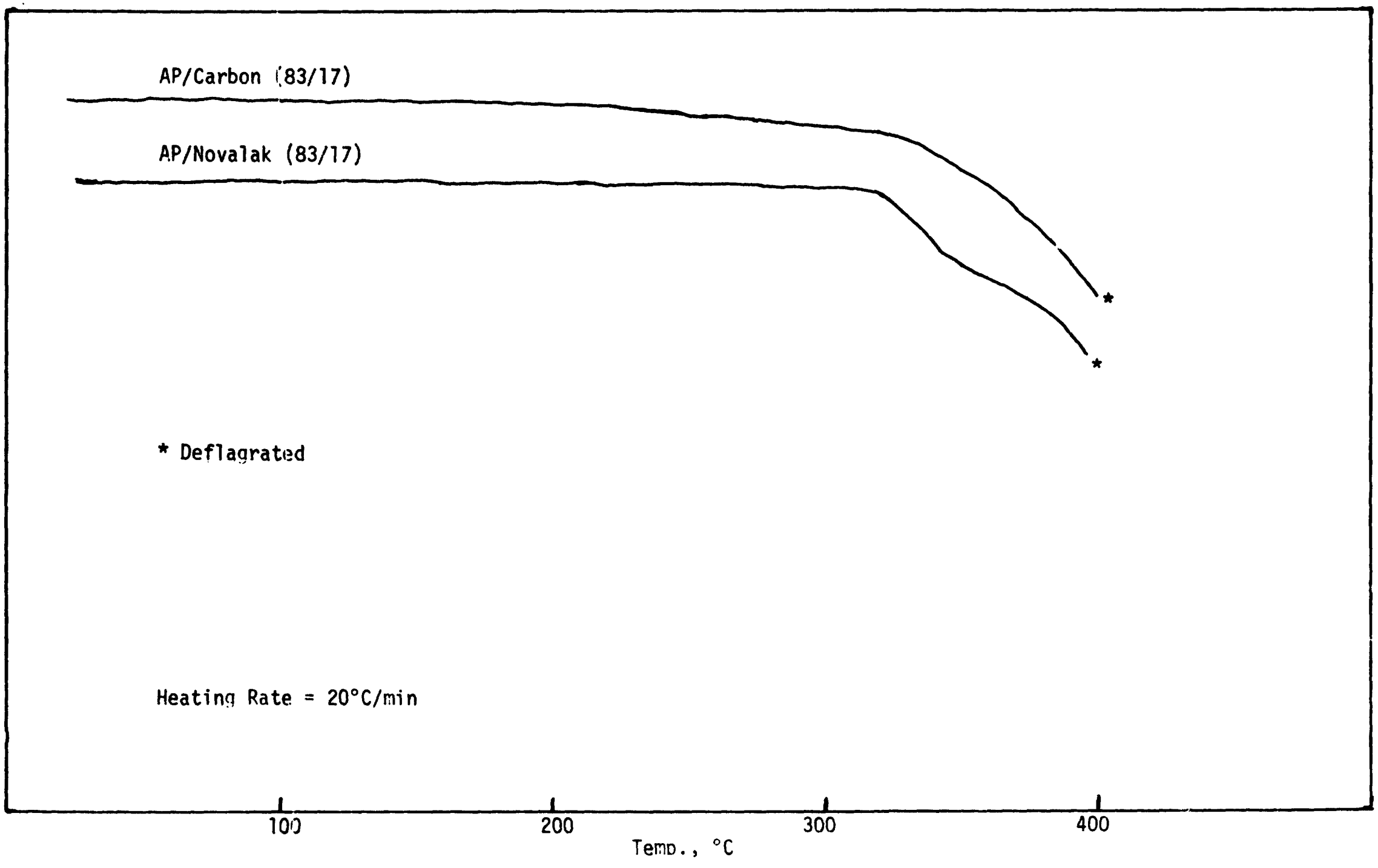
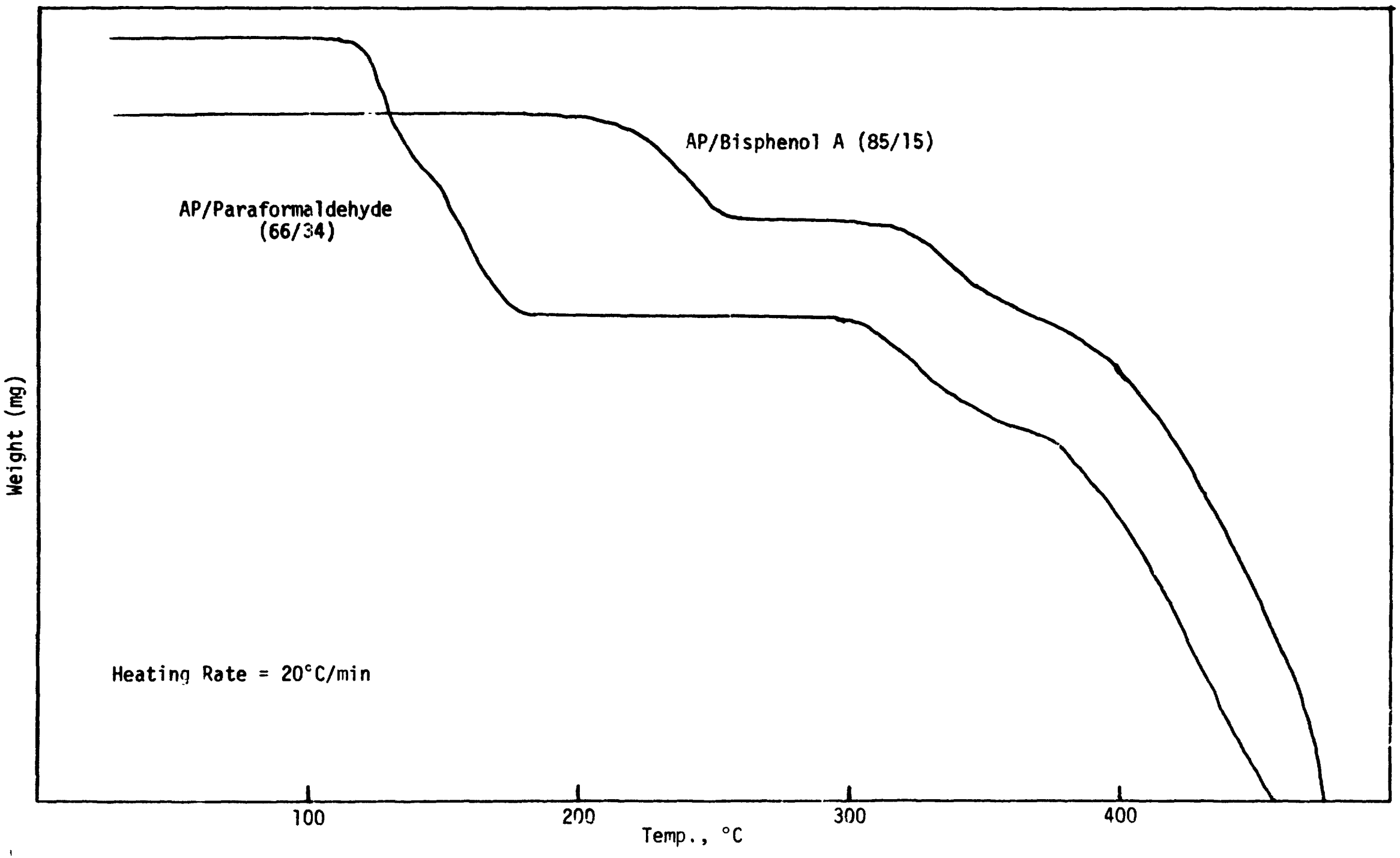


Figure 18

TGA'S OF AP WITH PARAFORMALDEHYDE AND WITH BISPHENOL A



BURNING RATES OBTAINED WITH PRESSED STRANDS OF AP
WITH NOVALAK, RESOLE, AND BISPHENOL A

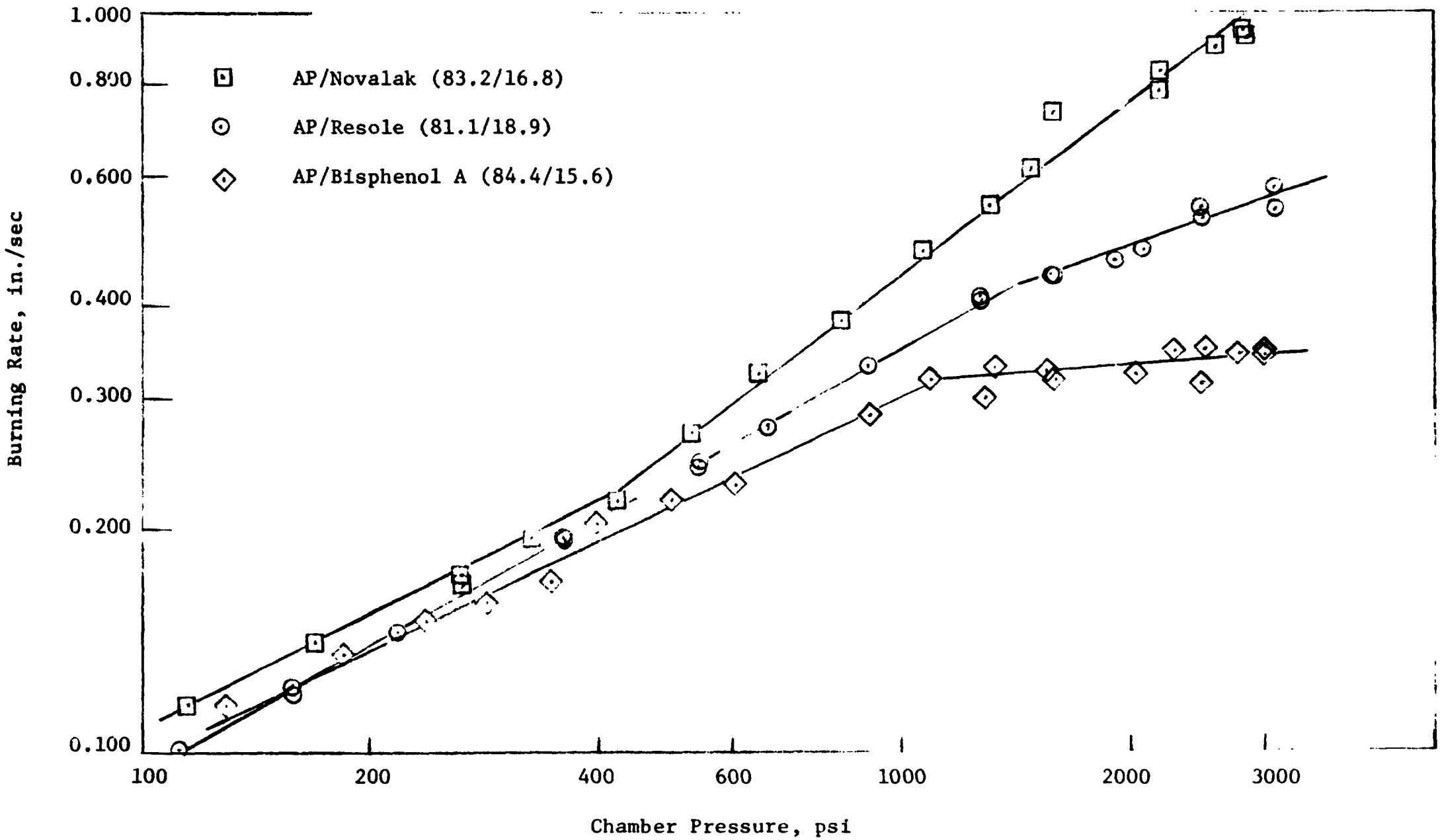


Figure 20

BURNING RATES OBTAINED WITH PRESSED STRANDS
OF AP/CARBON AND AP/PARAFORMALDEHYDE

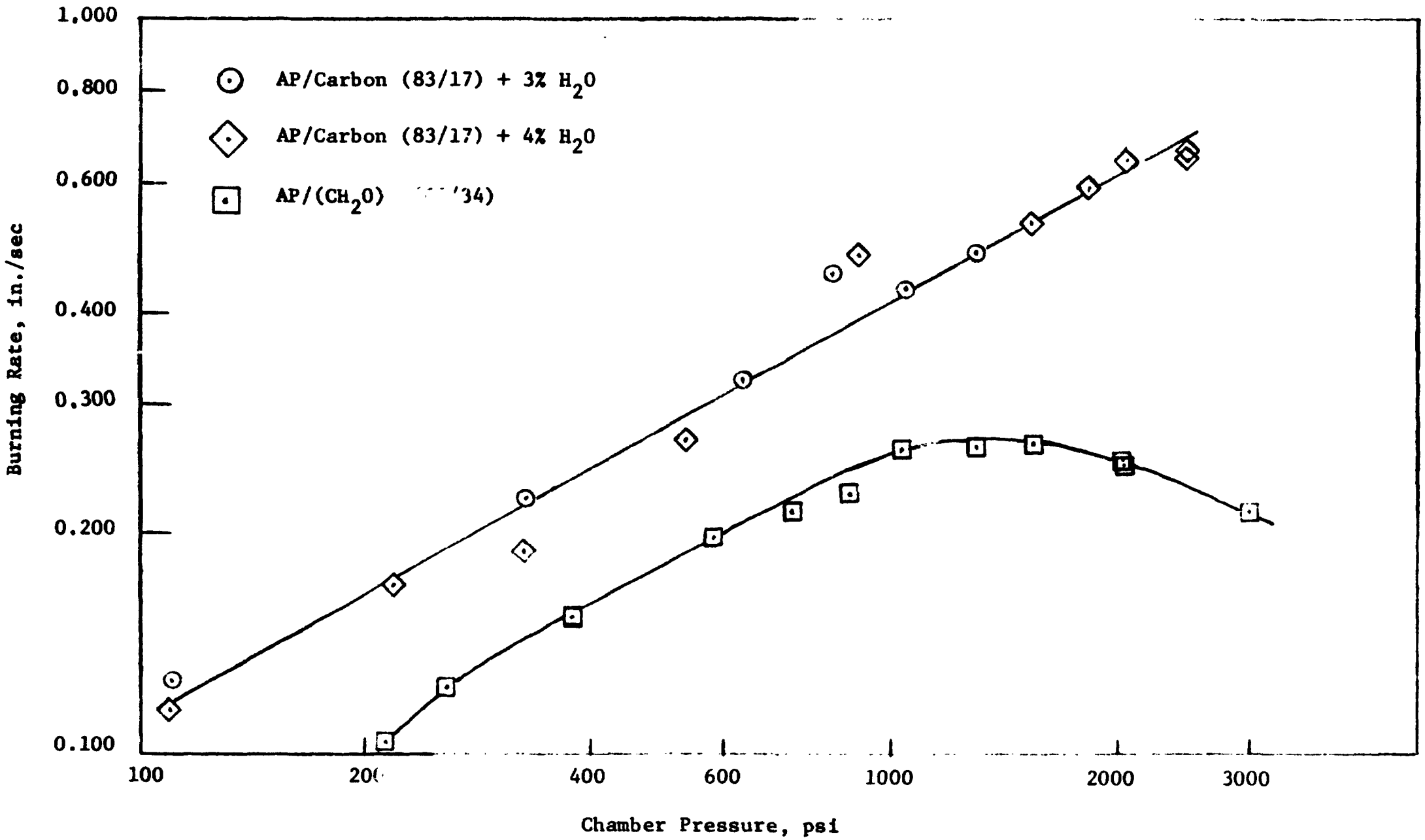
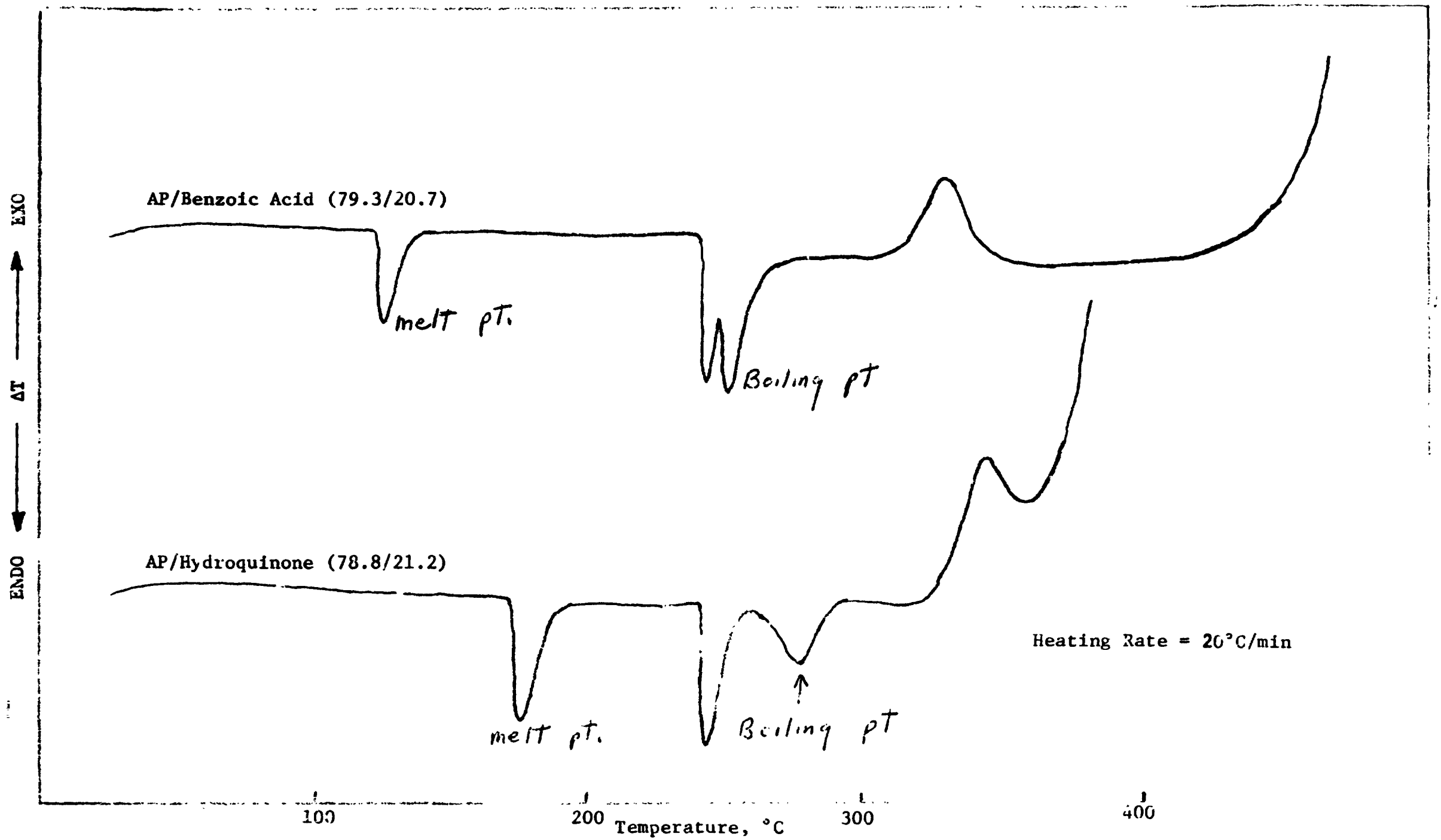


Figure 21

DTA's OF AP-BENZOIC ACID AND AP-HYDROQUINONE MIXTURES



BURNING RATES FOR PRESSED AP-BENZOIC ACID AND
AP HYDROQUINONE COMPOSITES

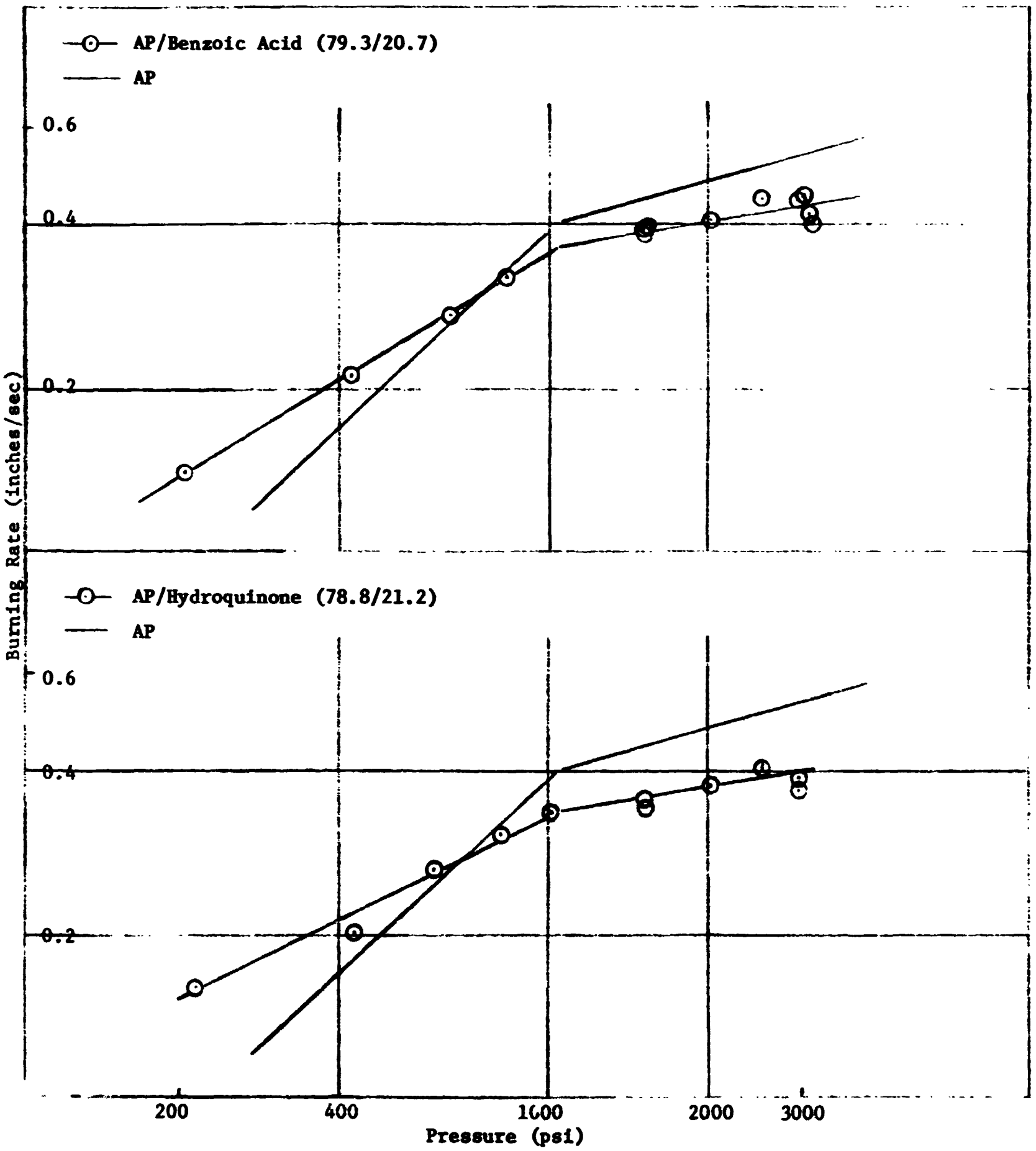


Figure 23

BURNING RATES OF AP-ALUMINUM AND AP-TRIPHENYLMEHANE COMPOSITES

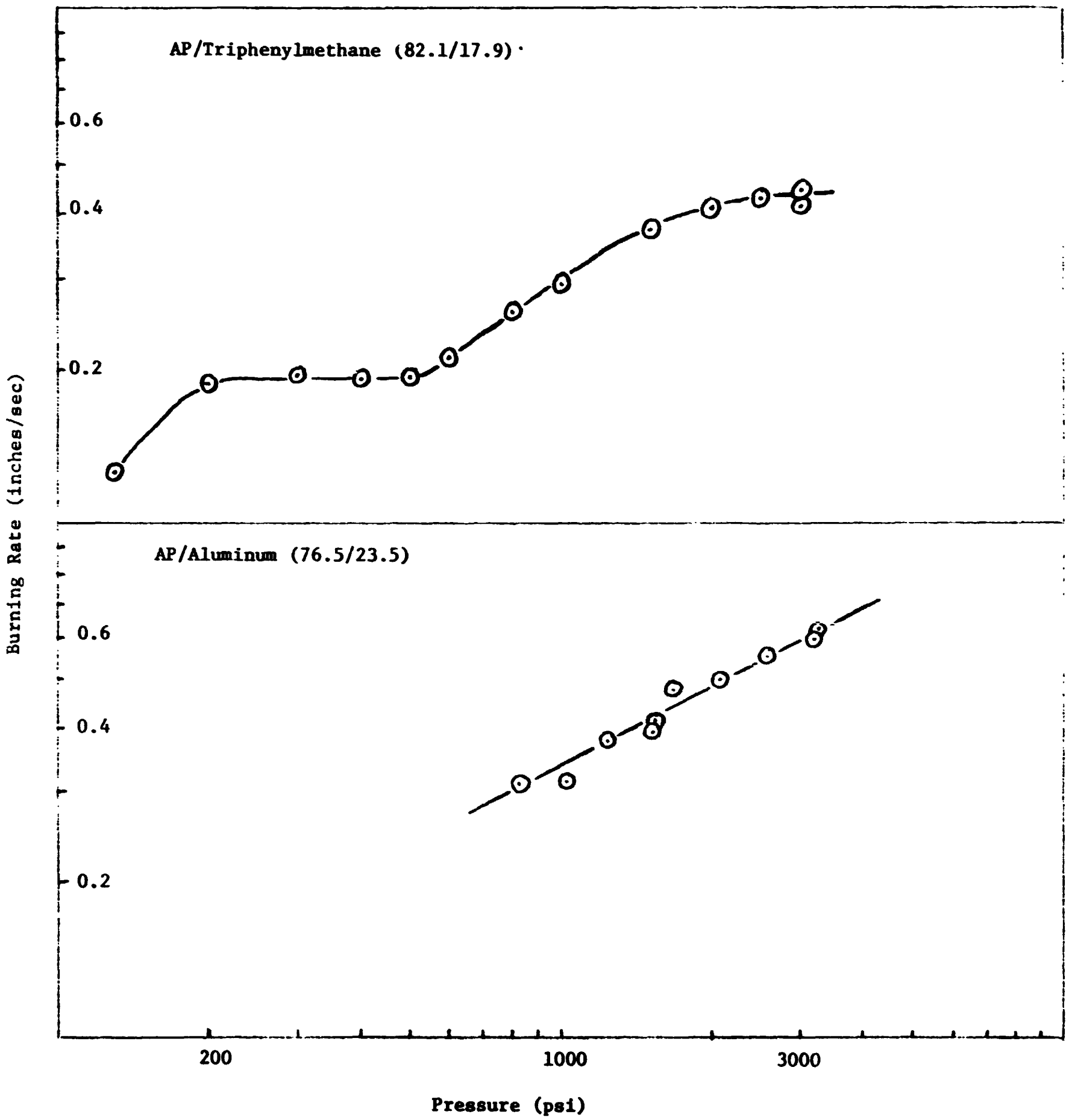


Figure 24

BURNING RATES OF COMPOSITES OF AP WITH BENZAMIDE,
ACETAMIDE AND ISOPHTHALONITRILE

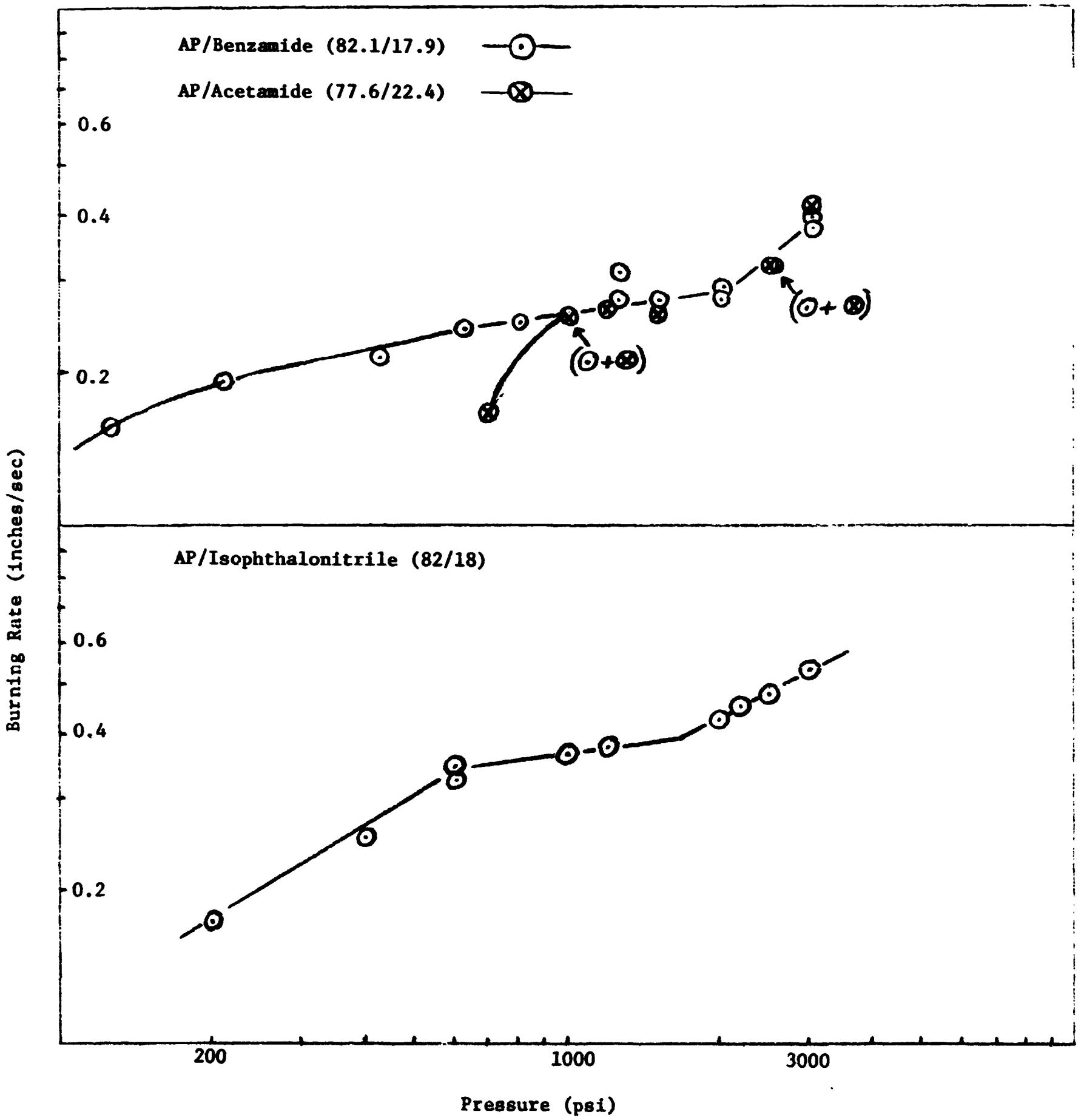
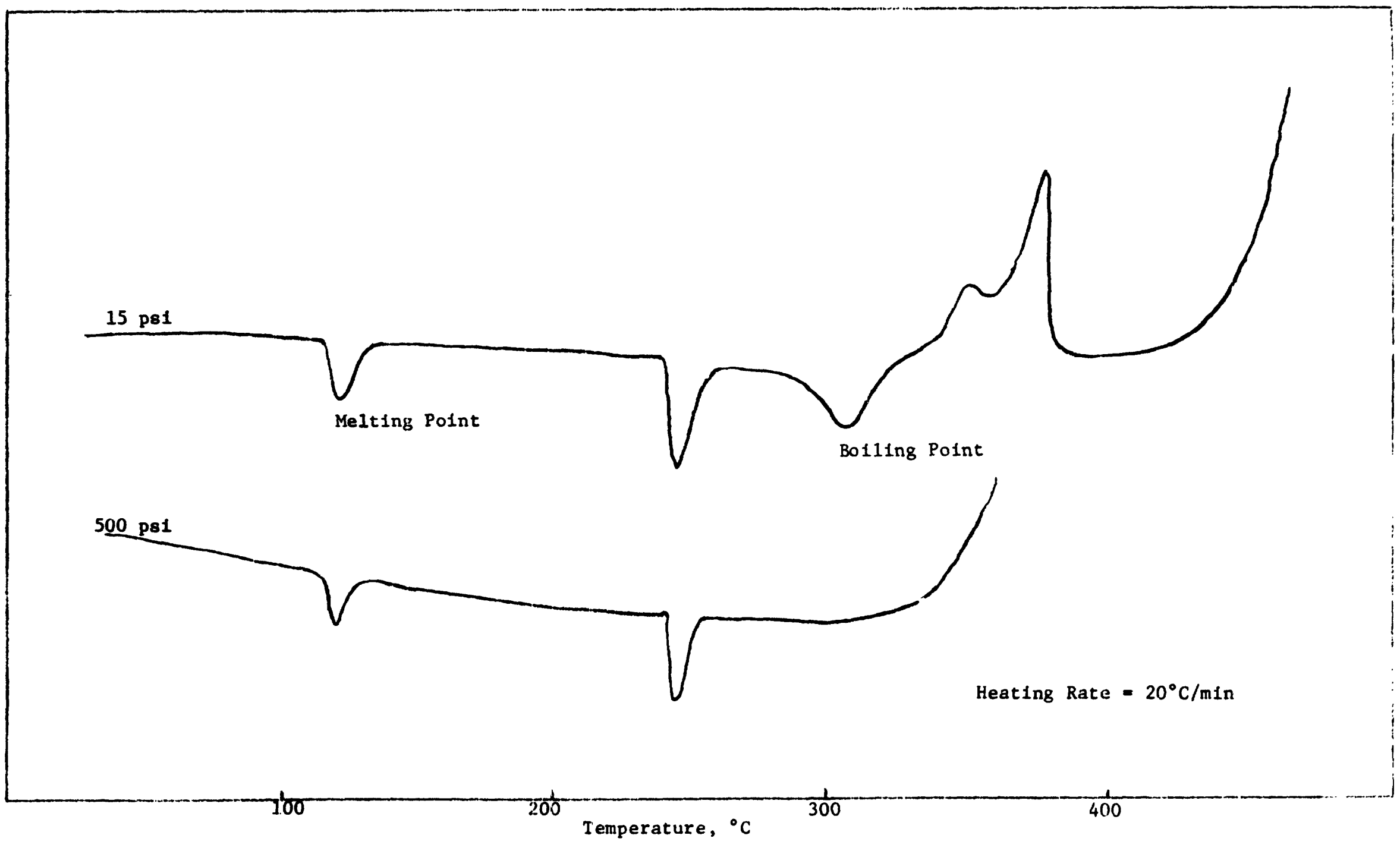
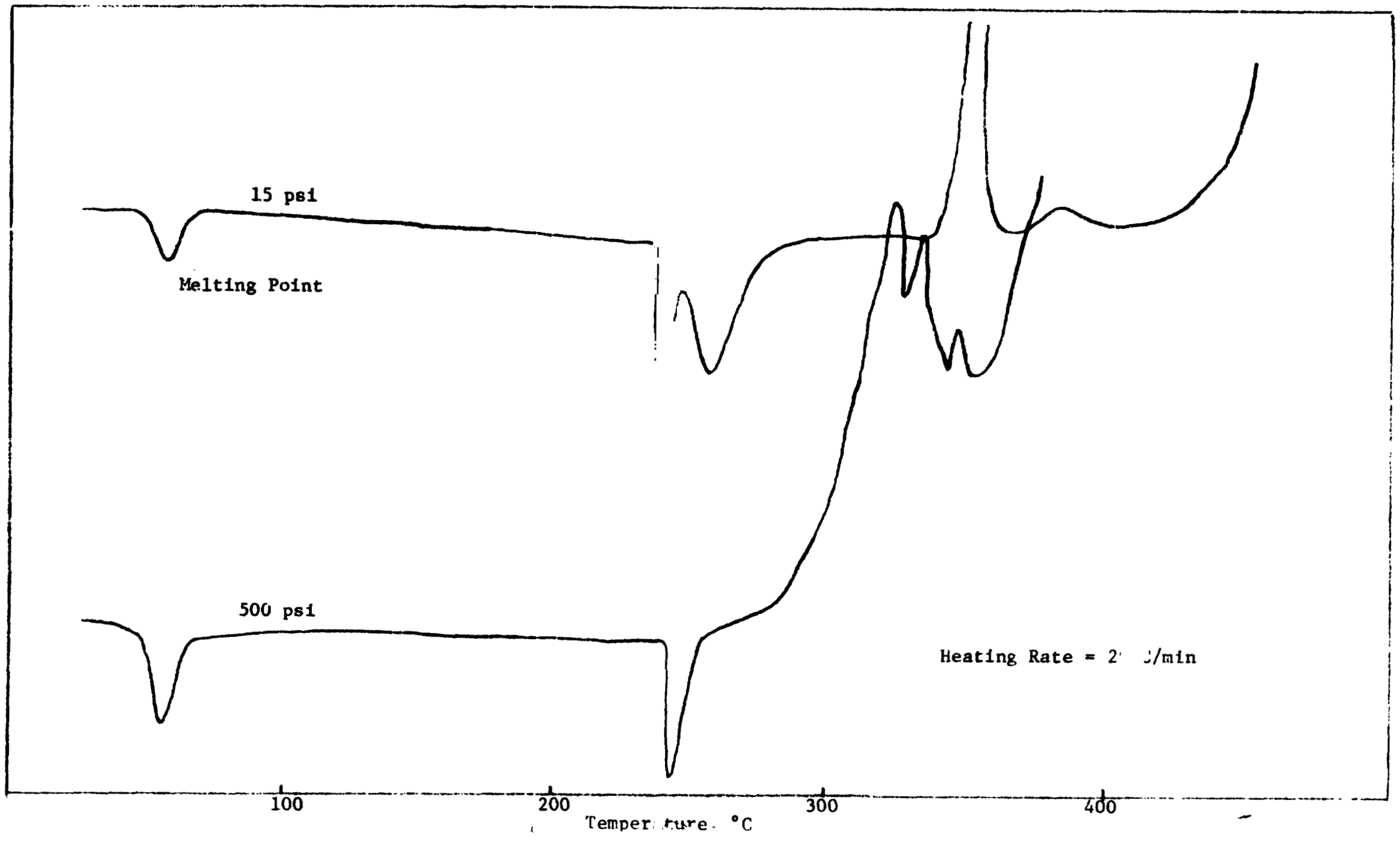


Figure 25

DTA's OF AP-BENZAMIDE AT 15 AND 500 PSI (NITROGEN)



DTA's OF AP-ACETAMIDE AT 15 AND 500 PSI (NITROGEN)



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BURNING RATES OF AP/SUCCINAMIDE COMPOSITES

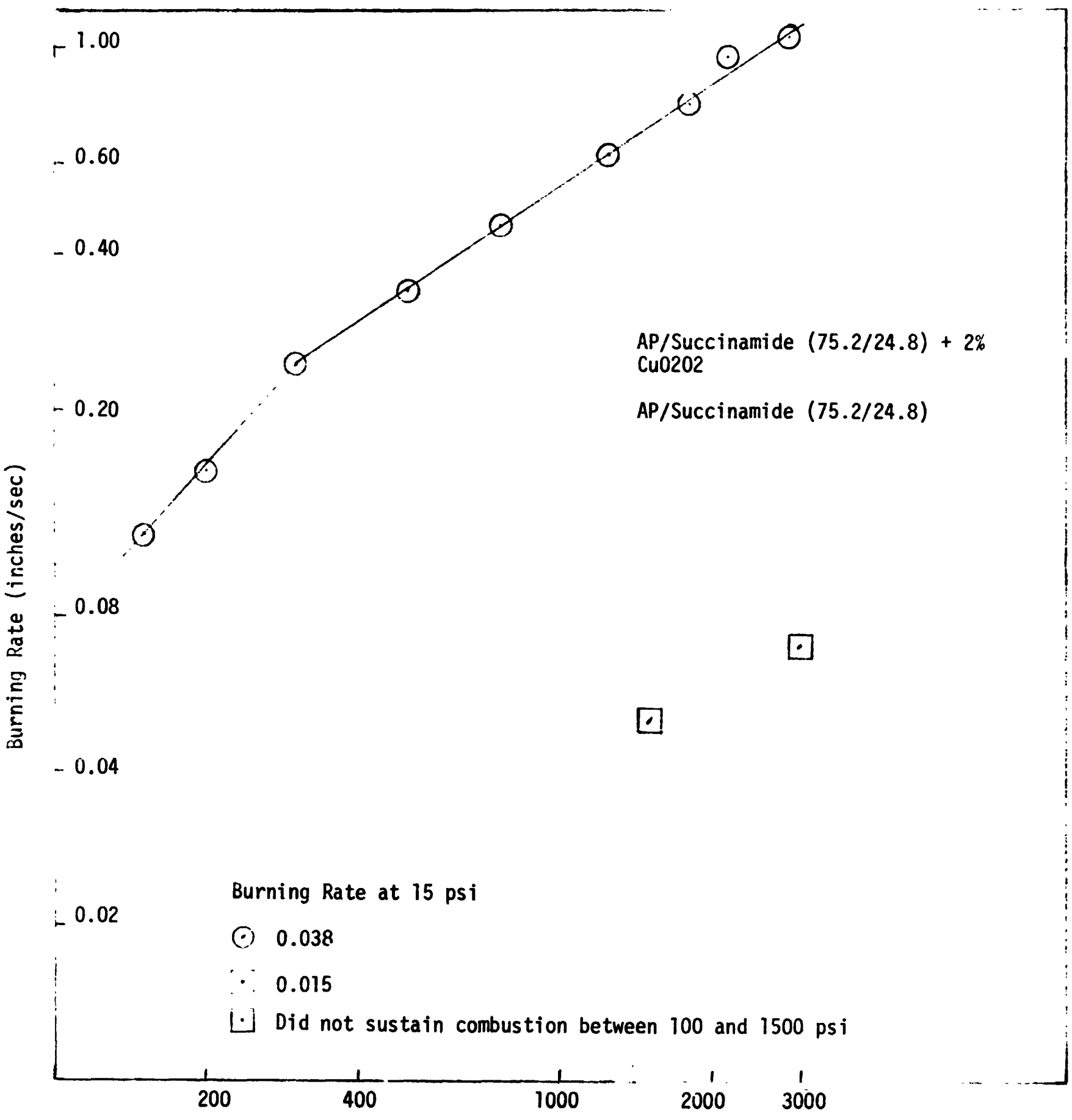
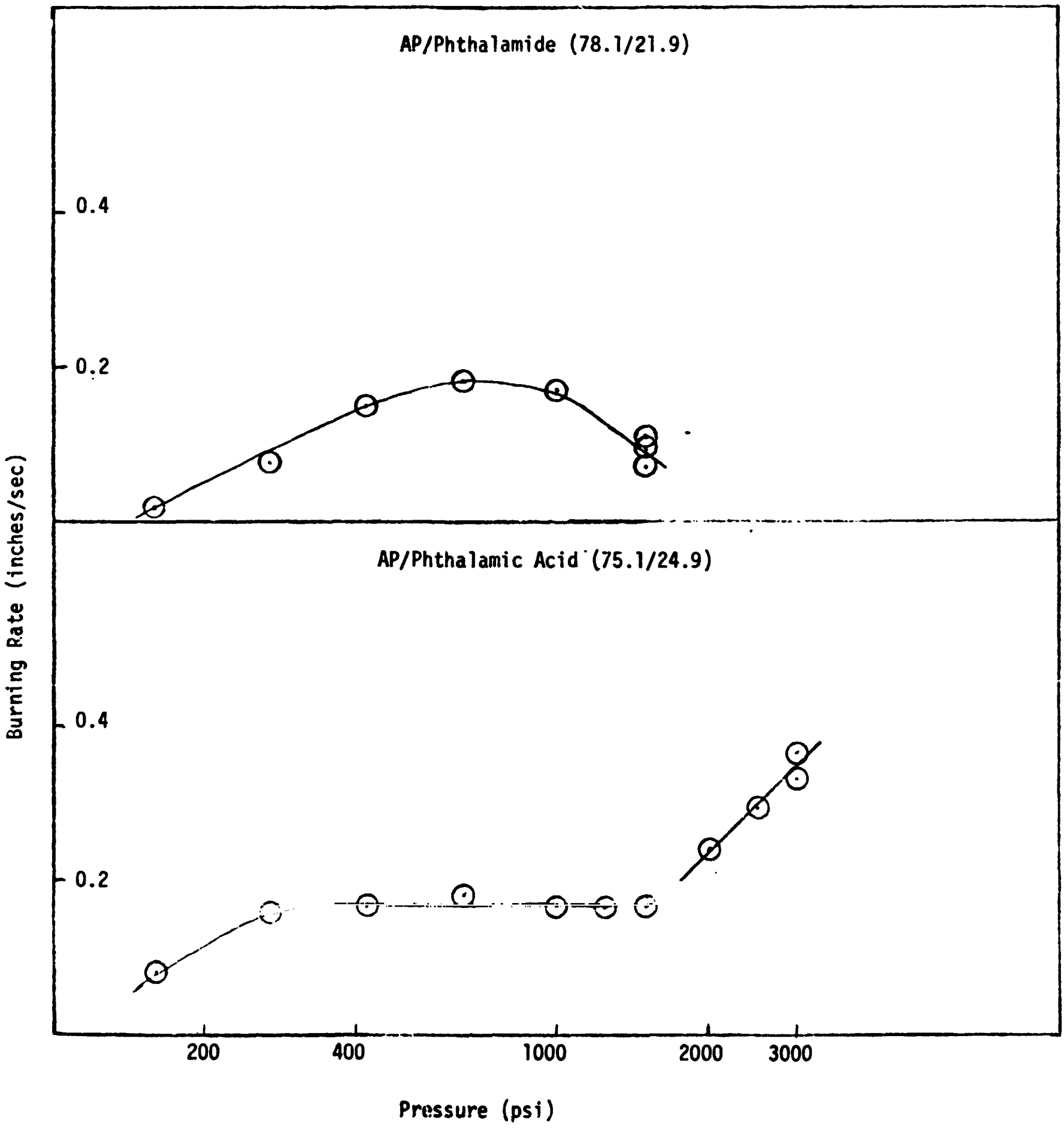
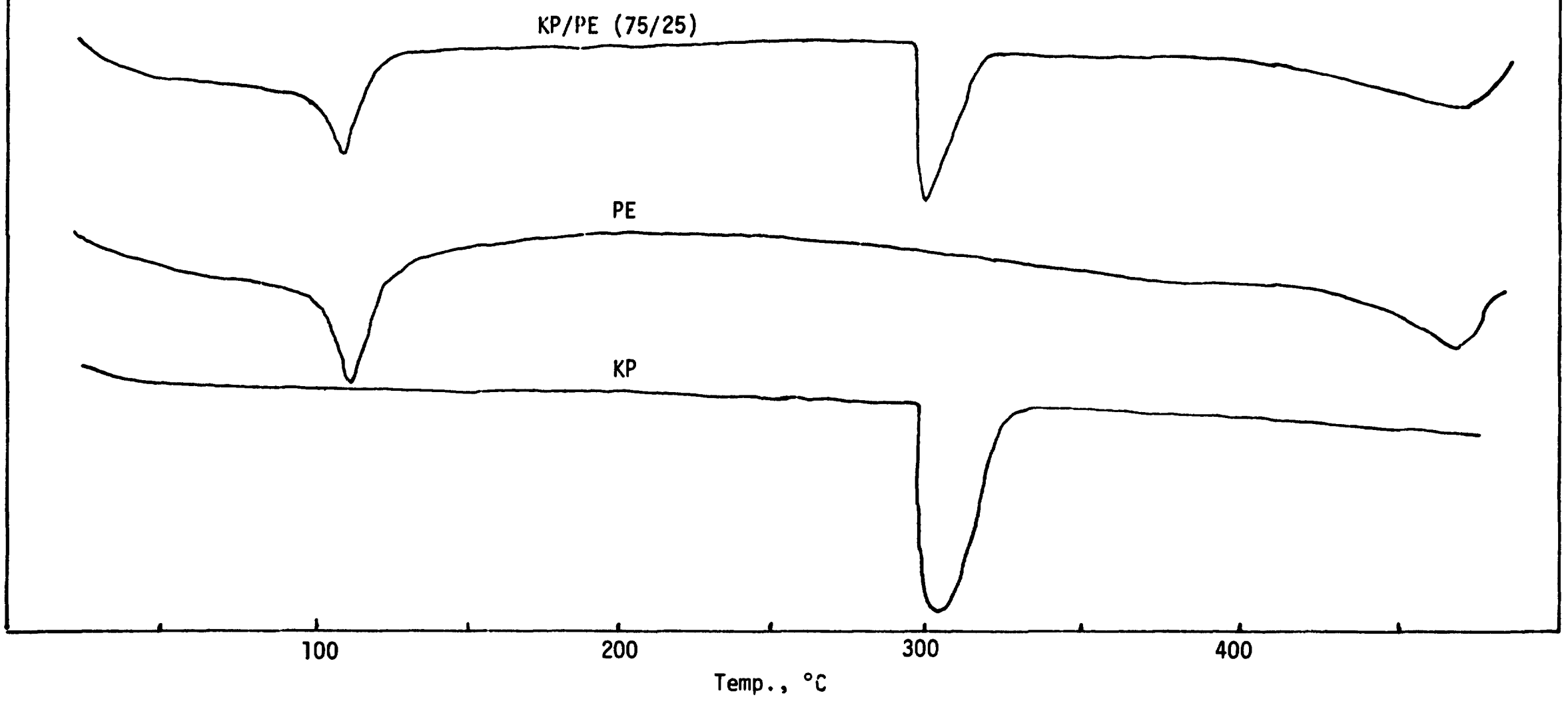


Figure 28

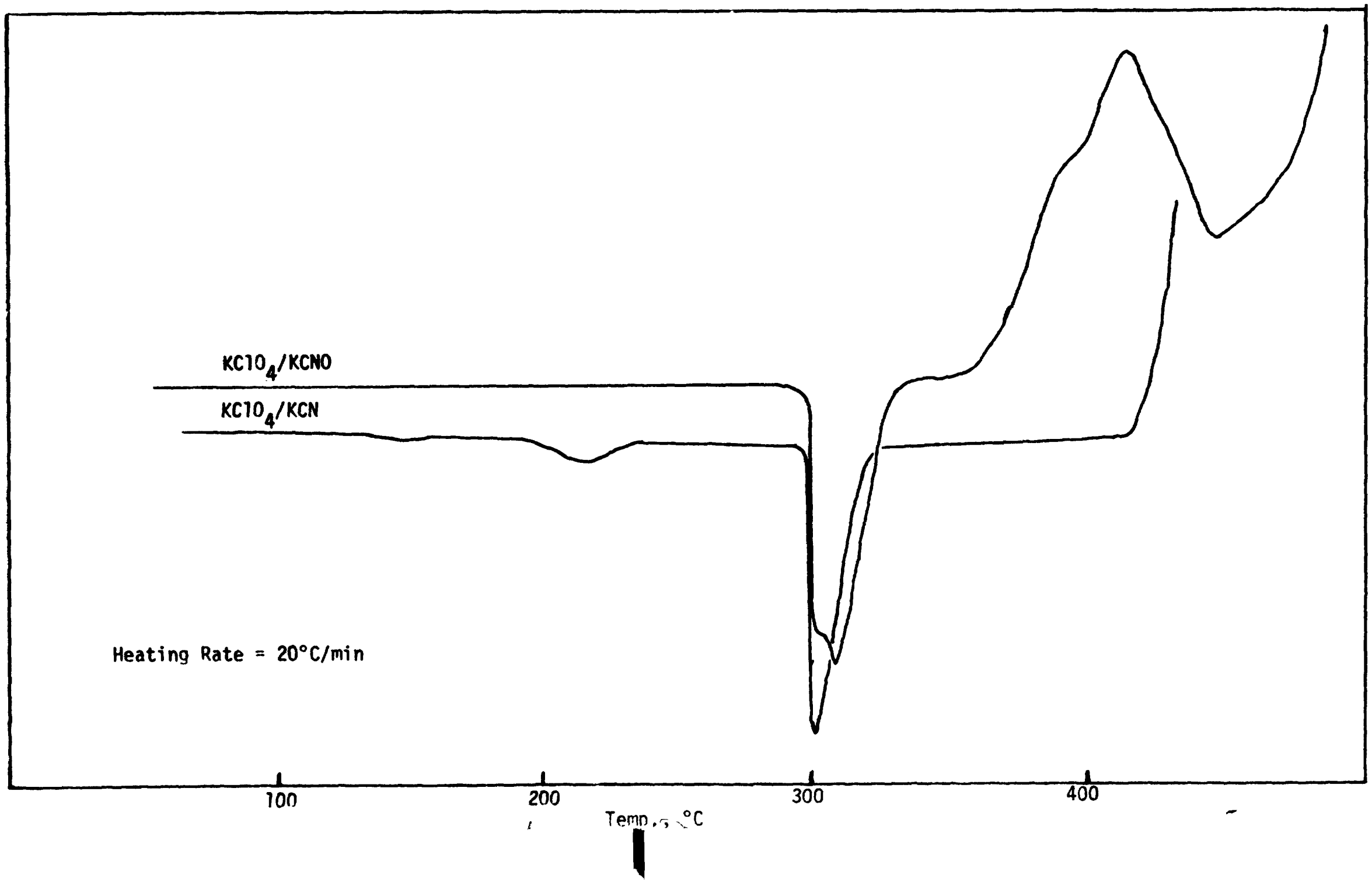
BURNING RATES OF AP/PHTHALAMIDE AND
AP/PHTHALAMIC ACID COMPOSITES



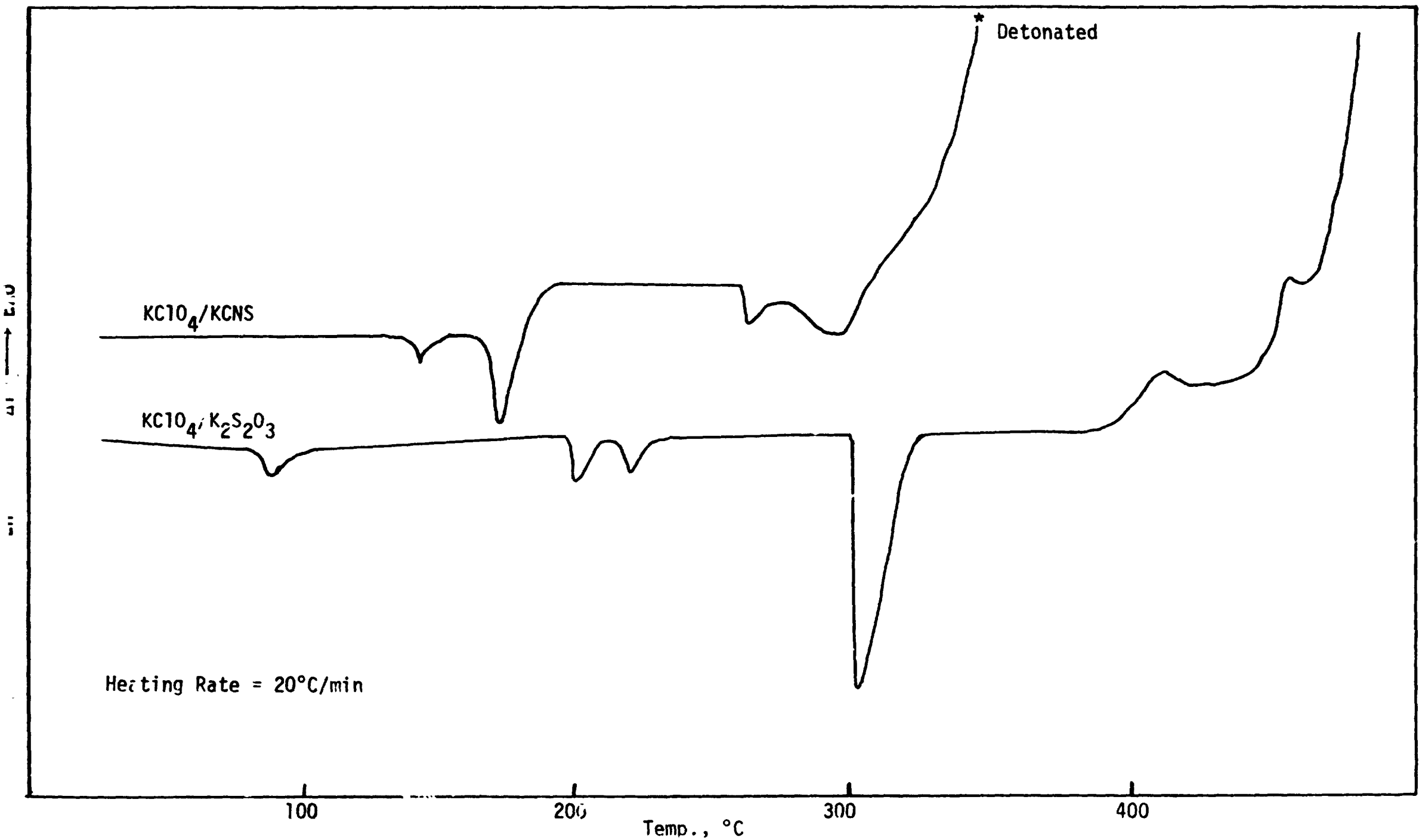
DTA THERMOGRAM OF POTASSIUM PERCHLORATE (KP), POLYETHYLENE (PE),
AND A MIXTURE OF KP AND PE



DTA'S OF 75/25 BLENDS OF $KClO_4$ WITH KCN AND KCNO



DTA'S OF 75/25 BLENDS OF $KClO_4$ WITH KCNS AND $K_2S_2O_3$



DTA'S OF $KClO_4$-COPPER OXIDE (80/20)